

SEARCH REQUEST FORM

Scientific and Technical Information Center

Requester's Full Name: Monique Cole Examiner #: 75037 Date: 9-10-03
 Art Unit: 1743 Phone Number 305-2447 Serial Number: 091921237
 Mail Box and Bldg/Room Location: 103 7-ECB Results Format Preferred (circle): PAPER DISK E-MAIL

If more than one search is submitted, please prioritize searches in order of need.

Please provide a detailed statement of the search topic, and describe as specifically as possible the subject matter to be searched. Include the elected species or structures, keywords, synonyms, acronyms, and registry numbers, and combine with the concept or utility of the invention. Define any terms that may have a special meaning. Give examples or relevant citations, authors, etc, if known. Please attach a copy of the cover sheet, pertinent claims, and abstract.

Title of Invention: Novel Aliphatic Compounds

Inventors (please provide full names): Marcus E. Ing. Wobrie

Earliest Priority Filing Date: 8-4-2000

For Sequence Searches Only Please include all pertinent information (parent, child, divisional, or issued patent numbers) along with the appropriate serial number.

Please search compound of claim 1 + its utility in perfumes (fragrance, odor, scent, smell, olfactory, etc.)

The particular compd. of claim 1 is representative of 16-member ~~aliphatic~~ aliphatic carbon compounds.

Please search specific compounds of claim 3 + processes of claims 6 + 7. Thank you.

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	Type of Search	Vendors and cost where applicable
Searcher: <u>EX</u>	NA Sequence (#) _____	STN <u>\$217.19</u>
Searcher Phone #: _____	AA Sequence (#) _____	Dialog _____
Searcher Location: _____	Structure (#) <u>(2)</u> <u>Questel/Orbit</u>	_____
Date Searcher Picked Up: _____	Bibliographic <u>Dr. Link</u>	_____
Date Completed: <u>9-12-03</u>	Litigation <u>Lexis/Nexis</u>	_____
Searcher Prep & Review Time: <u>1</u>	Fulltext _____	Sequence Systems _____
Clerical Prep Time: _____	Patent Family _____	WWW/Internet _____
Online Time: _____	Other _____	Other (specify) _____

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FILE 'REGISTRY' ENTERED AT 09:50:22 ON 12 SEP 2003
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FILE 'LREGISTRY' ENTERED AT 09:19:41 ON 12 SEP 2003
L1 STR

FILE 'REGISTRY' ENTERED AT 09:25:48 ON 12 SEP 2003
L2 0 S L1
L3 SCR 1898
L4 1 S L1 AND L3
L5 82 S L1 AND L3 FUL
SAV L5 COL237/A
L6 34 S L5 AND 2/O
L7 48 S L5 NOT L6
L8 1198588 S (C(L)H(L)P)/ELS

FILE 'LREGISTRY' ENTERED AT 09:34:27 ON 12 SEP 2003
E TRIMETHYLPHOSPHONIUM CHLORIDE/CN
L9 1 S E4

FILE 'REGISTRY' ENTERED AT 09:35:26 ON 12 SEP 2003
L10 426314 S L8 AND X/ELS
L11 10268 S L10 AND 4/ELC.SUB
L12 159741 S ?PHOSPHONI?/CNS
L13 60807 S L10 AND L12

FILE 'HCAPLUS' ENTERED AT 09:38:24 ON 12 SEP 2003
L14 167 S L6
L15 44 S L7
L16 60483 S L11 OR L13
L17 1 S L14 AND L16
L18 0 S L15 AND L17
L19 29 S L7/P
L20 17116 S WITTIG#
L21 8 S L14 AND L20
L22 64282 S ?PHOSPHONI?
L23 1 S L14 AND L22
L24 9 S L17 OR L21 OR L23
L25 27 S L19 NOT L24
L26 2 S L24 AND L15
L27 9 S L26 OR L24
L28 15 S L15 NOT (L27 OR L25)

FILE 'REGISTRY' ENTERED AT 09:50:22 ON 12 SEP 2003

FILE 'REGISTRY' ENTERED AT 09:51:00 ON 12 SEP 2003

A chemical structure of a six-membered ring. The ring consists of six carbon atoms. One carbon atom is double-bonded to an oxygen atom (C=O). Two of the carbon atoms are labeled 'G2'. The ring is numbered 1 through 6 in a clockwise direction starting from the carbon atom adjacent to the carbonyl group.

```
VAR G1=14/10
REP G2=(2-10) CH2
NODE ATTRIBUTES:
CONNECT IS E2 RC AT 1
CONNECT IS E2 RC AT 5
CONNECT IS E1 RC AT 11
DEFAULT MLEVEL IS ATOM
DEFAULT ECLEVEL IS LIMITED
```

GRAPH ATTRIBUTES:
RING(S) ARE ISOLATED OR EMBEDDED
NUMBER OF NODES IS 11

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STEREO ATTRIBUTES: NONE
L3          SCR 1898
L5          82 SEA FILE=REGISTRY SSS FUL L1 AND L3
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82 ANSWERS

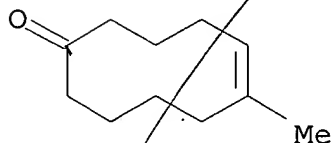
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FILE LAST UPDATED: 01 May 1997 (19970501/UP)

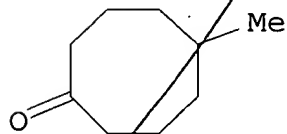
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L29 ANSWER 1 OF 6 CAOLD COPYRIGHT 2003 ACS on STN

AN CA60:13160c CAOLD
 TI bicyclo[2.1.1]hexanes
 AU Lowry, Betty R.
 TI synthesis and isomerization of some hexahydronaphthalenes
 AU Carnighan, Robert H.
 IT 92038-60-3 92286-92-5
 IT 92286-92-5
 RN 92286-92-5 CAOLD
 CN 5-Cyclodecen-1-one, 6-methyl- (7CI, 9CI) (CA INDEX NAME)

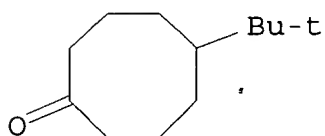


L29 ANSWER 2 OF 6 CAOLD COPYRIGHT 2003 ACS on STN
 AN CA60:419a CAOLD
 TI diketone condensation of cyclohexanone with homologs of HCHO - (III)
 AU Tilichenko, M. N.
 IT 933-11-9 1502-38-1 1614-94-4 2544-00-5 3137-39-1
 4103-10-0 4457-72-1 4744-89-2 13152-05-1 13152-06-2
 13152-07-3 13366-81-9 14252-11-0 21406-47-3 21406-49-5
 22460-44-2 22575-90-2 24133-19-5 24133-20-8 28399-91-9
 38433-06-6 38451-99-9 39565-62-3 41416-37-9 50615-08-2
 58768-92-6 58768-93-7 63821-83-0 73674-39-2 86162-28-9
 90645-57-1 90646-99-4 90676-27-0 90676-28-1 91010-22-9
 91010-30-9 91251-52-4 91351-32-5 91351-33-6 91351-34-7
 91367-49-6 92057-86-8 92057-87-9 92316-88-6 92369-25-0
 92377-28-1 93571-61-0 93571-62-1 94673-06-0 95430-64-1
 97194-84-8 98511-35-4 98562-28-8 98562-29-9 100336-27-4
 106424-73-1
 IT 38451-99-9
 RN 38451-99-9 CAOLD
 CN Cyclooctanone, 5-methyl- (7CI, 9CI) (CA INDEX NAME)

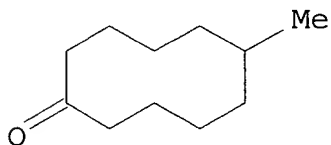


L29 ANSWER 3 OF 6 CAOLD COPYRIGHT 2003 ACS on STN
 AN CA59:6270a CAOLD
 TI conformational analysis - (XXVI) stereochem. studies of the cyclooctane ring
 AU Allinger, Norman L.; Greenberg, S.

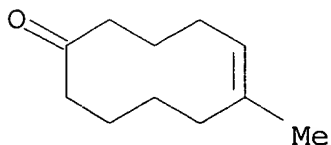
IT 10217-58-0 15300-02-4 **15753-46-5** 34680-83-6 42084-95-7
88828-80-2 88828-81-3 91242-63-6 91337-20-1 91688-77-6
91693-90-2 92031-40-8 92039-12-8 92106-86-0 92111-56-3
92158-46-8 92857-63-1 93991-21-0 94382-56-6 94441-46-0
97029-37-3 97499-36-0 100194-58-9 103622-81-7
IT **15753-46-5**
RN 15753-46-5 CAOLD
CN Cyclooctanone, 5-(1,1-dimethylethyl)- (9CI) (CA INDEX NAME)



L29 ANSWER 4 OF 6 CAOLD COPYRIGHT 2003 ACS on STN
AN CA57:5819a CAOLD
TI stereospecific synthesis of 6-methyl-trans-5-cyclodecenone
AU Wharton, Peter S.
IT 6134-91-4 **76393-81-2** 91213-20-6 91369-92-5
92286-92-5 96621-33-9 98693-95-9 98782-27-5
IT **76393-81-2 92286-92-5**
RN 76393-81-2 CAOLD
CN Cyclodecanone, 6-methyl- (6CI, 7CI, 9CI) (CA INDEX NAME)

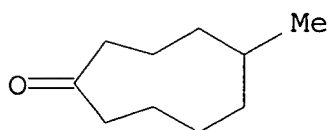


RN 92286-92-5 CAOLD
CN 5-Cyclodecen-1-one, 6-methyl- (7CI, 9CI) (CA INDEX NAME)

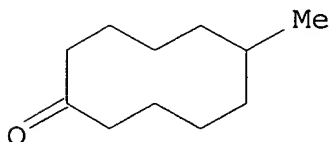


L29 ANSWER 5 OF 6 CAOLD COPYRIGHT 2003 ACS on STN
AN CA52:10914b CAOLD
TI many-membered C rings - (XVI) acetolysis of 5,5-dimethylcyclononanol tosylate
AU Blomquist, Alfred T.; Meinwald, Y. C.

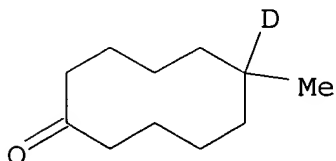
IT 3618-11-9 22748-23-8 53262-23-0 58746-32-0 **80926-31-4**
80926-32-5 91459-00-6 99992-88-8 101873-99-8 103984-03-8
104068-41-9 106949-65-9 108474-06-2
IT **80926-31-4**
RN 80926-31-4 CAOLD
CN Cyclononanone, 5-methyl- (6CI, 9CI) (CA INDEX NAME)



L29 ANSWER 6 OF 6 CAOLD COPYRIGHT 2003 ACS on STN
AN CA51:3475g CAOLD
TI C ring - (LXX) transannular displacements in the cyclodecane series
AU Prelog, Vladimir; Kueng, W.
IT 37520-32-4 **76393-81-2** 99992-37-7 100048-41-7 100248-19-9
100248-28-0 100533-86-6 100534-06-3 100538-52-1 101865-04-7
105207-58-7 105838-43-5 107779-51-1 **108845-61-0**
108993-65-3 109017-98-3 112420-39-0 114555-09-8
IT **76393-81-2 108845-61-0**
RN 76393-81-2 CAOLD
CN Cyclodecanone, 6-methyl- (6CI, 7CI, 9CI) (CA INDEX NAME)



RN 108845-61-0 CAOLD
CN Cyclodecanone-6-d, 6-methyl- (6CI) (CA INDEX NAME)



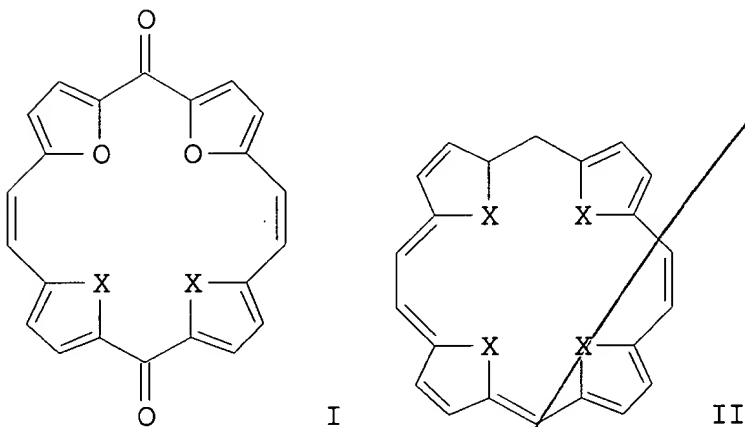
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=> d 127 1-9 cbib abs hitstr hitind

L27 ANSWER 1 OF 9 HCAPLUS COPYRIGHT 2003 ACS on STN
 1994:106965 Document No. 120:106965 Porphyrinoid [22]annulenoquinones.
 Maerkl, Gottfried; Striebl, Ulrich (Inst. Org. Chem., Univ.
 Regensburg, Regensburg, D-93040, Germany). Angewandte Chemie,
 105(9), 1387-90 (See also Angew. Chem., Int. Ed. Engl., 1993, 32(9),
 1333-5) (German) 1993. CODEN: ANCEAD. ISSN: 0044-8249. OTHER
 SOURCES: CASREACT 120:106965.

GI



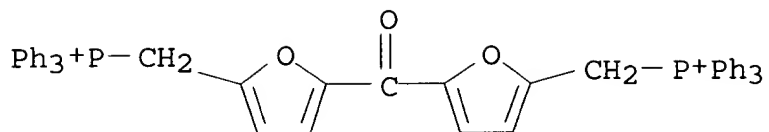
AB The synthesis of diketones I (X = oxygen, sulfur) derived from [20]porphyrin(1.3.13) 22- π -II (X = -NH-, :N-) was reported. I can be characterized as [22]annulenoquinones. In soln. I exhibits spectral characteristics that indicate the presence of a dynamic structure.

IT 37893-23-5P

(prepn. of, as intermediate for [22]annulenoquinone)

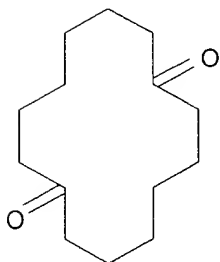
RN 37893-23-5 HCAPLUS

CN Phosphonium, [carbonylbis(5,2-furandiylmethylene)]bis[triphenyl-,
 dichloride (9CI) (CA INDEX NAME)



● 2 Cl⁻

IT 152637-02-0
 (redn. potential in comparison to [22]annulenoquinone)
 RN 152637-02-0 HCAPLUS
 CN Cyclotetradecatetraenediyn-1,8-dione, bis(1,1-dimethylethyl)- (9CI)
 (CA INDEX NAME)
 CM 1
 CRN 152637-01-9
 CMF C22 H40 O2
 CCI IDS



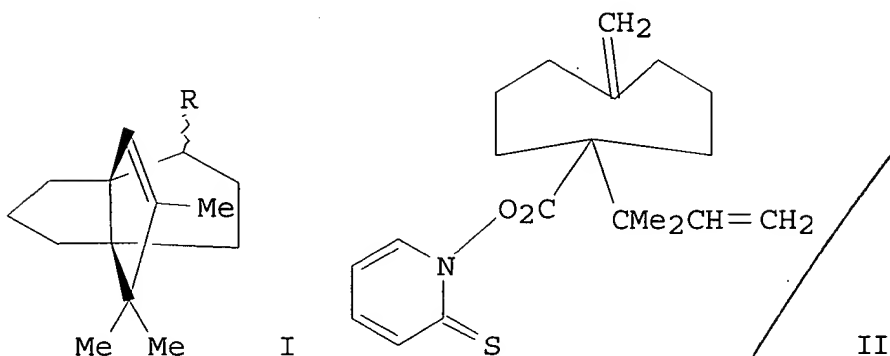
2 (D1-Bu-t)

CC 28-23 (Heterocyclic Compounds (More Than One Hetero Atom))
 Section cross-reference(s): 22, 75
 IT 35050-48-7P 37893-23-5P 52157-61-6P
 (prepn. of, as intermediate for [22]annulenoquinone)
 IT 152637-02-0 152637-06-4, Cyclooctadecatetraenetetrayne-1,6-
 dione
 (redn. potential in comparison to [22]annulenoquinone)

L27 ANSWER 2 OF 9 HCAPLUS COPYRIGHT 2003 ACS on STN
 1993:213305 Document No. 118:213305 Tandem transannular radical
 cyclizations. Total syntheses of (.+-.)-modhephene and
 (.+-.)-epi-modhephene. Curran, Dennis P.; Shen, Wang (Dep. Chem.,

Univ. Pittsburgh, Pittsburgh, PA, 15260, USA). Tetrahedron, 49(4), 755-70 (English) 1993. CODEN: TETRAB. ISSN: 0040-4020. OTHER SOURCES: CASREACT 118:213305.

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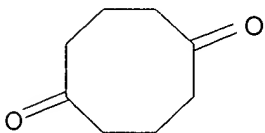


AB Modhephene (I; R = .alpha.-Me) and epi-modhephene (I; R = .beta.-Me) have been synthesized by a new tandem transannular radical cyclization strategy. The key tandem cyclization is conducted by the Barton thiohydroxamate method with an exo(methylene)cyclooctane (II).

IT 1489-74-3, 1,5-Cyclooctanedione
(Wittig ethylidenation of)

RN 1489-74-3 HCAPLUS

CN 1,5-Cyclooctanedione (7CI, 8CI, 9CI) (CA INDEX NAME)

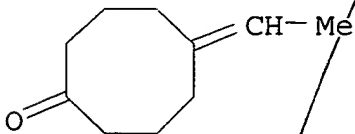


IT 147163-27-7P

(prepn. and condensation of, with prenylmagnesium chloride)

RN 147163-27-7 HCAPLUS

CN Cyclooctanone, 5-ethylidene- (9CI) (CA INDEX NAME)



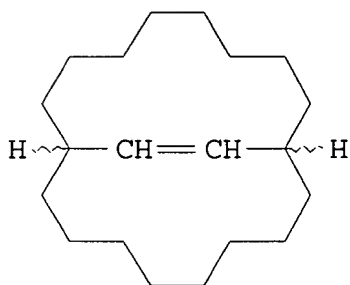
CC 30-15 (Terpenes and Terpenoids)

IT 1489-74-3, 1,5-Cyclooctanedione
(Wittig ethylidenation of)

IT 124770-01-0P 147163-34-6P
 (prepn. and Wittig methylenation of)
 IT 147163-27-7P
 (prepn. and condensation of, with prenylmagnesium chloride)

L27 ANSWER 3 OF 9 HCAPLUS COPYRIGHT 2003 ACS on STN
 1992:83255 Document No. 116:83255 Stereoisomers of
 bicyclo[8.8.2]icos-19-ene: synthesis, novel properties, and
 molecular mechanics calculations. Macomber, Roger S.; Rardon,
 Daniel E.; Emge, Thomas J. (Dep. Chem., Univ. Cincinnati,
 Cincinnati, OH, 45221-0172, USA). Journal of Organic Chemistry,
 57(2), 433-4 (English) 1992. CODEN: JOCEAH. ISSN: 0022-3263.
 OTHER SOURCES: CASREACT 116:83255.

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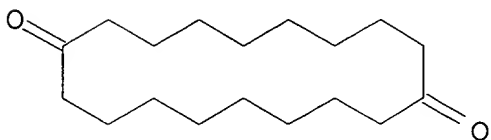
AB The title compd. (1) has been prepd. in modest yield as a mixt. of four stereoisomers. The synthetic sequence involved conversion of 1,10-cyclooctadecadione to 1,10-dimethylenecyclooctadecane via a Wittig reaction, hydroboration/oxidn. of the latter to 1,10-bis(hydroxymethyl)cyclooctadecane (4), and PCC oxidn. of 4 to 1,10-cyclooctadecanedicarboxaldehyde (5), an unstable compd. prone to air oxidn. to 1,10-cyclooctadecanedicarboxylic acid (6). Both 4 and 5 (and presumably 6) were formed as mixts. of cis and trans diastereomers. McMurry carbonyl coupling of 5 led to 1 as a mixt. of two major and two minor stereoisomers. While the minor isomers react with Br₂, the major isomers do not. The major isomers of 1 are therefore assigned structures with a trans double bond, and either trans (1e) or cis (1c) methine hydrogens. In such structures the .pi.-bond is located in the interior of the mol. and is sterically protected by the eighteen membered ring. The minor isomers are assigned structures with a cis double bond and cis (inside, 1b) or trans (1d) methine hydrogens. In the latter two structures the .pi.-bond is located on the accessible exterior of the mol., with the greatest degree of exposure in 1b. Mol. mechanics calcns. predict the following order of calcd. min. energy of the stereoisomers of 1 (energies in kcal/mol): cis,cis (outside) 1a (59.77) > 1d (52.41) > 1c (52.58) > 1e (47.94) > 1b (45.19). The

barrier for rotation of the C₂H₂ bridge of 1e or 1c into the mean plane of the 18-membered ring, which allows limited access to the .pi.-bond, is calcd. to be 20 kcal/mol.

IT 13747-10-9, 1,10-Cyclooctadecanedione
(Wittig reaction of, with methylenetriphenylphosphorane)

RN 13747-10-9 HCAPLUS

CN 1,10-Cyclooctadecanedione (6CI, 9CI) (CA INDEX NAME)



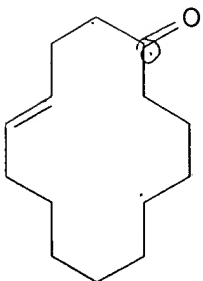
CC 24-7 (Alicyclic Compounds)
Section cross-reference(s): 22

IT 3487-44-3
(Wittig reaction of, with cyclooctadecadione)

IT 13747-10-9, 1,10-Cyclooctadecanedione
(Wittig reaction of, with methylenetriphenylphosphorane)

L27 ANSWER 4 OF 9 HCAPLUS COPYRIGHT 2003 ACS on STN
1988:221317 Document No. 108:221317 Free-radical macrocyclization-transannular cyclization. Porter, Ned A.; Chang, Vincent H. T.; Magnin, David R.; Wright, Bruce T. (Dep. Chem., Duke Univ., Durham, NC, 27706, USA). Journal of the American Chemical Society, 110(11), 3554-60 (English) 1988. CODEN: JACSAT. ISSN: 0002-7863. OTHER SOURCES: CASREACT 108:221317.

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14 member

I

AB Intramol. free-radical addn. to olefins substituted with electron-withdrawing groups has been studied. The free radicals are generated from the corresponding iodides by reaction with Bu₃SnH or

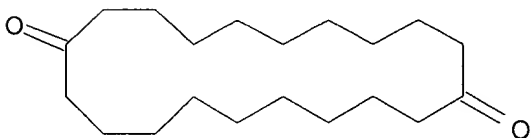
Bu₃SnCl/NaBH₃CN. Macrocyclic compds. of 12-20 members are generated by this procedure in good yield, and while endocyclization is favored, exocyclization can be forced if 1,1-dicyano-substituted olefins are used. Macrocyclization-transannular cyclization sequences are possible if the transannular cyclization is 5-exo. Fused bicyclic [9.3.0] systems have been prepd., and other [n.3.0] systems should be available by this approach. Two-step cyclization sequences have also been investigated. The macrocycle is generated in one free-radical-mediated step, and the transannular cyclization is then achieved in a second free-radical reaction. Thus, Bu₃SnH mediated free radical cyclization of I(CH₂)₇CH:CHCH₂CH₂C(O)CH:CH₂ gave 80% macrocycle I. Rates of transannular 5-exo-cyclizations in 14-membered rings are .apprx.10⁴ s⁻¹.

IT 38734-07-5P

(prepn. of)

RN 38734-07-5 HCAPLUS

CN 1,11-Cycloeicosanedione (6CI, 9CI) (CA INDEX NAME)



CC 24-6 (Alicyclic Compounds)

IT 928-80-3P 3603-99-4P 38734-07-5P 56606-79-2P

101999-70-6P 101999-71-7P 114157-31-2P 114157-32-3P

114157-33-4P 114157-44-7P 114157-50-5P 114183-78-7P

114183-79-8P 114247-44-8P

(prepn. of)

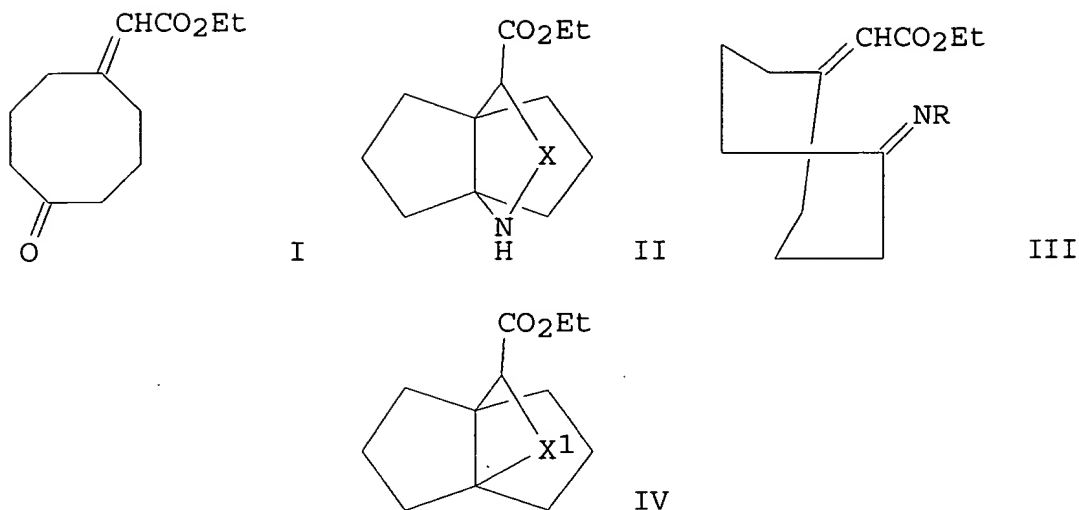
IT 54005-84-4

(reaction of, with Wittig reagent)

L27 ANSWER 5 OF 9 HCAPLUS COPYRIGHT 2003 ACS on STN

1987:407179 Document No. 107:7179 Synthesis of heterocyclic propellanes. Preparation and transannular reactions of 5-[(ethoxycarbonyl)methylene]cyclooctanone and the corresponding oximes and hydrazones. Malamidou-Xenikaki, E.; Nicolaides, D. N. (Lab. Org. Chem., Univ. Thessaloniki, Thessaloniki, Greece). Tetrahedron, 42(18), 5081-8 (English) 1986. CODEN: TETRAB. ISSN: 0040-4020. OTHER SOURCES: CASREACT 107:7179.

GI

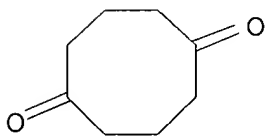


AB Methylenecyclooctanone I was prepd. by Wittig monoolefination of cyclooctane-1,5-dione with $\text{Ph}_3\text{P}:\text{CHCO}_2\text{Et}$. The reactions of I with $\text{NH}_2\text{OH}.\text{HCl}$ and PhNHNH_2 gave diazapropellanes II ($\text{X} = \text{O}$, NPh), resp. via thermal transannular cyclization. Photolysis of I, oxime III ($\text{R} = \text{OMe}$), and hydrazone III ($\text{R} = \text{NMe}_2$) gave oxapropellane IV ($\text{X1} = \text{O}$) and azapropellanes IV ($\text{X1} = \text{NOMe}$, NNMe_2), resp. N-Acetylated derivs. are also prepd. from II ($\text{X} = \text{O}$, NPh).

IT 1489-74-3, Cyclooctane-1,5-dione
(Wittig reaction of, with ethoxycarbonylmethylenetriphenylphosphorane)

RN 1489-74-3 HCAPLUS

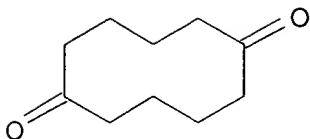
CN 1,5-Cyclooctanedione (7CI, 8CI, 9CI) (CA INDEX NAME)



IT 38734-05-3, Cyclodecane-1,6-dione
(Witting reaction of, with ethoxycarbonylmethylenetriphenylphosphorane)

RN 38734-05-3 HCAPLUS

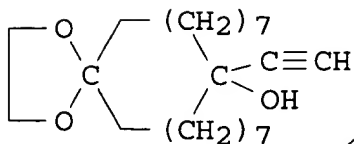
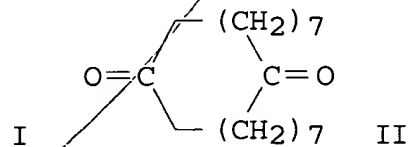
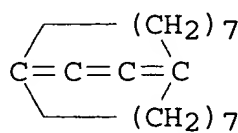
CN 1,6-Cyclodecanedione (6CI, 9CI) (CA INDEX NAME)



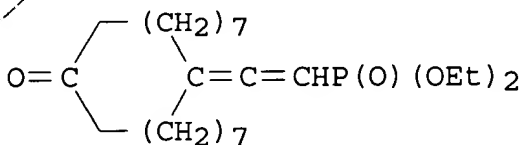
- CC 28-23 (Heterocyclic Compounds (More Than One Hetero Atom))
- ST **Wittig** cyclooctanedione cyclodecanedione
ethoxycarbonylmethylenetriphenylphosphorane; cycloaddn photochem
ethoxycarbonylmethylenecyclooctanone oxime hydrazone; azapropellane
methoxyethoxycarbonyl; oxapropellane ethoxycarbonyl; diazapropellane
phenylethoxycarbonyl; bicyclodecanol ethoxycarbonylmethylene;
oxaazapropellane acetylethoxycarbonyl; propellane heterocyclic
- IT **Wittig** reaction
(of cycloalkanediones with ethoxycarbonylmethylenetriphenylphosphorane)
- IT 1099-45-2
(**Wittig** reaction of, with cycloalkanediones)
- IT 1489-74-3, Cyclooctane-1,5-dione
(**Wittig** reaction of, with ethoxycarbonylmethylenetriphenylphosphorane)
- IT 38734-05-3, Cyclodecane-1,6-dione
(**Wittig** reaction of, with ethoxycarbonylmethylenetriphenylphosphorane)

L27 ANSWER 6 OF 9 HCAPLUS COPYRIGHT 2003 ACS on STN
1986:88172 Document No. 104:88172 Synthetic approaches to molecules
with sterically hidden functional groups. 2. Bicyclo[8.8.2]eicosa-
1(19),10(20),19-triene: the first bicyclic cumulatriene. Macomber,
Roger S.; Hemling, Thomas C. (Dep. Chem., Univ. Cincinnati,
Cincinnati, OH, 45221, USA). Journal of the American Chemical
Society, 108(2), 343-4 (English) 1986. CODEN: JACSAT. ISSN:
0002-7863. OTHER SOURCES: CASREACT 104:88172.

GI



III



IV

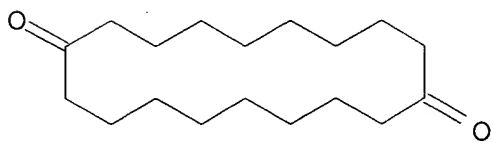
AB An 8-step synthesis of the title compd. (I) from 1,10-cyclooctadecanedione (II) is reported. The sequence involved protection of one of the carbonyls in II using an indirect approach of **Wittig** mono-olefination, ketal formation, and ozonolysis. The resulting monoketone was treated with $\text{LiC.tplbond.CSiMe}_3$ and then desilylated to give the hydroxy ethynyl ketal III. Treatment of III with $(\text{EtO})_2\text{PCl}$, then mild hydrolysis of the ketal, gave allenic phosphonate IV, which afforded I when treated with $(\text{Me}_2\text{CH})_2\text{NLi}$. The phys. and spectral data for I and its precursors are reported.

IT 13747-10-9

(Wittig reaction of)

RN 13747-10-9 HCAPLUS

CN 1,10-Cyclooctadecanedione (6CI, 9CI) (CA INDEX NAME)

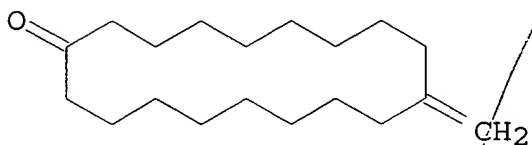


IT 99605-57-9P

(prepn. and ketalization of)

RN 99605-57-9 HCAPLUS

CN Cyclooctadecanone, 10-methylene- (9CI) (CA INDEX NAME)



IT 99605-66-0P

(prepn. of)

RN 99605-66-0 HCAPLUS

CN Cyclooctadecanone, 10-ethynyl-10-hydroxy- (9CI) (CA INDEX NAME)



CC 24-7 (Alicyclic Compounds)

IT 13747-10-9

(Wittig reaction of)

IT 3487-44-3
(Wittig reaction of, with cyclooctadecanedione)
IT 99605-57-9P
(prepn. and ketalization of)
IT 99605-59-1P 99605-65-9P 99605-66-0P 99605-67-1P
(prepn. of)

L27 ANSWER 7 OF 9 HCAPLUS COPYRIGHT 2003 ACS on STN
1975:530678 Document No. 83:130678 Transannular electronic interactions between nonconjugated groups 1,6-dimethylenecyclodecane, and its synthesis. Koli, Andrew K. (South Carolina State Coll., Orangeburg, SC, USA). Journal of the Indian Chemical Society, 51(12), 1012-14 (English) 1974. CODEN: JICSAH. ISSN: 0019-4522.

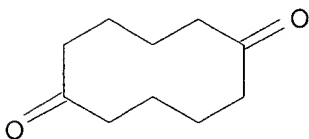
GI For diagram(s), see printed CA Issue.

AB Naphthalene was treated 20 hr with Li in PrNH₂ to give 89% I, which heated 6 hr at 45.degree. with HCO₂H-H₂O₂ gave 80% II. Oxidn. of II with Pb(OAc)₄ in C₆H₆ gave 87% III, which with Ph₃P:CH₂ gave 83% of the title compd. (IV). The uv of IV exhibited a .pi.-.pi.* band at 256 nm with .epsilon. 500 l. mole⁻¹ cm⁻¹. The flexibility of the ring of IV allowed the nonconjugated double bonds to come together in a conformation resembling s-cis-butadiene and the orbitals mixed.

IT 38734-05-3P
(prepn. and Wittig reaction of, with triphenylphosphorane)

RN 38734-05-3 HCAPLUS

CN 1,6-Cyclodecanedione (6CI, 9CI) (CA INDEX NAME)



CC 22-2 (Physical Organic Chemistry)

IT 38734-05-3P

(prepn. and Wittig reaction of, with triphenylphosphorane)

L27 ANSWER 8 OF 9 HCAPLUS COPYRIGHT 2003 ACS on STN
1975:155482 Document No. 82:155482 Transannular addition to 1,5-dimethylenecyclooctane. Bishop, Roger (Dep. Chem., Univ. Stirling, Stirling, UK). Journal of the Chemical Society, Perkin Transactions 1: Organic and Bio-Organic Chemistry (1972-1999) (20), 2364-7 (English) 1974. CODEN: JCPRB4. ISSN: 0300-922X.

GI For diagram(s), see printed CA Issue.

AB Oxidn. of 9-oxabicyclo[3.3.1]nonan-1-ol gave 83% cyclooctane-1,5-dione which with Ph₃P:CH₂ gave 42% 1,5-dimethylenecyclooctane (I). I with HCl, and AcOH gave the bicyclo[3.3.1]nonane derivs. II and III resp. previously assigned

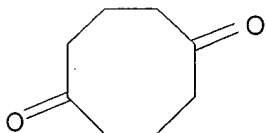
(Baggaley, K. H., et al, 1968) as the bicyclo[3.3.2]decanes IV and V, resp.

IT 1489-74-3P

(prepn. and Wittig reaction with
methyltriphenylphosphonium bromide)

RN 1489-74-3 HCAPLUS

CN 1,5-Cyclooctanedione (7CI, 8CI, 9CI) (CA INDEX NAME)



CC 24-6 (Alicyclic Compounds)

IT 1489-74-3P

(prepn. and Wittig reaction with
methyltriphenylphosphonium bromide)

L27 ANSWER 9 OF 9 HCAPLUS COPYRIGHT 2003 ACS on STN

1969:412639 Document No. 71:12639 Rearrangement of
1,2-divinyl-1,2-cyclooctanediol. A ring expansion by four carbons.
Marvell, Elliot N.; Tao, Terisa (Oregon State Univ., Corvallis, OR,
USA). Tetrahedron Letters (17), 1341-2 (English) 1969. CODEN:
TELEAY. ISSN: 0040-4039.

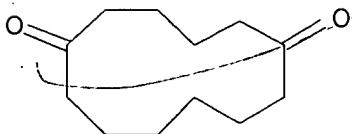
AB Oxidn. of cyclooctanone according to Wittig and Krebs gave
an impure 1,2-cyclooctanedione (I) contg. various impurities
including cyclooctanone and a substance showing the presence of a
strong ir OH band. The crude I dried over CaCl₂, treated with an
excess of H₂C:CHMgBr in tetrahydrofuran, and the product isolated by
preparative gas chromatog. gave 1,2-divinyl-1,2-cyclooctanediol
(II), m. 35-7.degree., characterized by ir and N.M.R. spectra. II
in cyclohexane heated 12 hrs. in a sealed tube at 225.degree.
yielded 40-50%, 1,6-cyclododecanedione (III); orange
bis(dinitrophenylhydrazine) m. 268-72.degree.. Wolff-Kishner redn.
of III gave cyclododecane. It is suggested that the rapid
conversion of a cyclic bis-enol to an aldol product is peculiar to
the medium rings.

IT 10329-89-2P

(prepn. of)

RN 10329-89-2 HCAPLUS

CN 1,6-Cyclododecanedione (6CI, 8CI, 9CI) (CA INDEX NAME)



CC 24 (Alicyclic Compounds)

IT 10329-89-2P 22733-78-4P
(prepn. of)

=> d 125 1-27 cbib abs hitstr hitrn

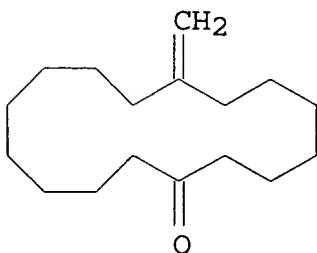
L25 ANSWER 1 OF 27 HCAPLUS COPYRIGHT 2003 ACS on STN
2002:122927 Document No. 136:183552 Novel macrocyclic ketones as odor enhancers in perfume compositions. Eh, Marcus; Woehrle, Ingo (Haarmann & Reimer G.m.b.H., Germany). PCT Int. Appl. WO 2002012157 A1 20020214, 42 pp. DESIGNATED STATES: W: AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DZ, EC, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, TZ, UA, UG, US, UZ, VN, YU, ZA, ZW, AM, AZ, BY, KG, KZ, MD, RU, TJ, TM; RW: AT, BE, BF, BJ, CF, CG, CH, CI, CM, CY, DE, DK, ES, FI, FR, GA, GB, GR, IE, IT, LU, MC, ML, MR, NE, NL, PT, SE, SN, TD, TG, TR. (German). CODEN: PIXXD2. APPLICATION: WO 2001-EP8471 20010723. PRIORITY: DE 2000-10038021 20000804.

AB Novel alkylidenecyclohexadecanones or alkylcyclohexadecenones were prepd. These compds. comprise valuable odorous substances contg. a touch of muscone which enables the prodn. of perfumes enhanced with the novel odorous touch. Thus, 1,9-cyclohexadecanedione was converted to its monoethyleneacetal which was methylenated, followed by acetal hydrolysis and isomerization to give 9-methyl-8-cyclohexadecenone. The latter compd. added a musk note to perfume compns.

IT 398509-41-6P 398509-46-1P
(novel macrocyclic ketones as odor enhancers in perfume compns.)

RN 398509-41-6 HCAPLUS

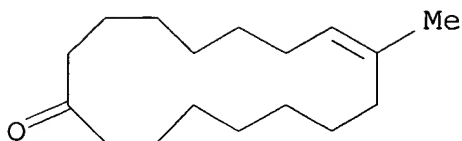
CN Cyclohexadecanone, 8-methylene- (9CI) (CA INDEX NAME)



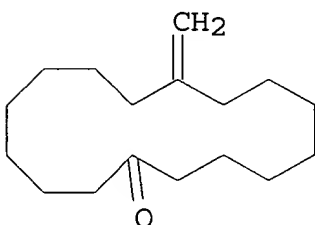
Applicant

RN 398509-46-1 HCAPLUS

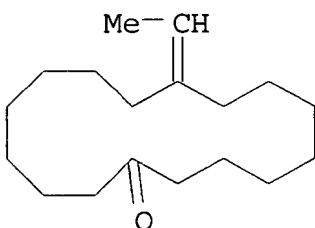
CN 8-Cyclohexadecen-1-one, 9-methyl- (9CI) (CA INDEX NAME)



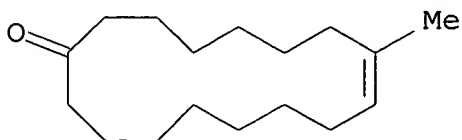
IT 398509-40-5P 398509-45-0P
 (novel macrocyclic ketones as odor enhancers in perfume compns.)
 RN 398509-40-5 HCAPLUS
 CN Cyclohexadecanone, 9-methylene- (9CI) (CA INDEX NAME)



RN 398509-45-0 HCAPLUS
 CN Cyclohexadecanone, 9-ethylidene- (9CI) (CA INDEX NAME)

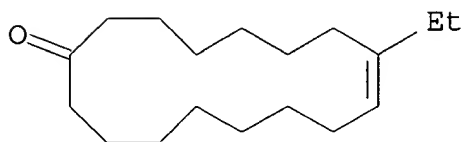


IT 398509-47-2P 398509-48-3P 398509-49-4P
 398509-50-7P 398509-51-8P 398509-52-9P
 398509-54-1P
 (novel macrocyclic ketones as odor enhancers in perfume compns.)
 RN 398509-47-2 HCAPLUS
 CN 8-Cyclohexadecen-1-one, 8-methyl- (9CI) (CA INDEX NAME)



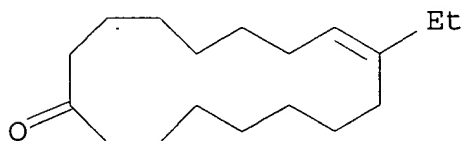
RN 398509-48-3 HCAPLUS

CN 8-Cyclohexadecen-1-one, 8-ethyl- (9CI) (CA INDEX NAME)



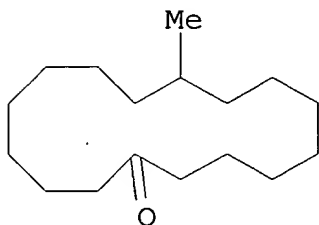
RN 398509-49-4 HCAPLUS

CN 8-Cyclohexadecen-1-one, 9-ethyl- (9CI) (CA INDEX NAME)



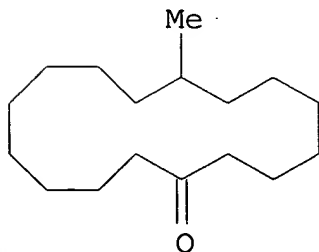
RN 398509-50-7 HCAPLUS

CN Cyclohexadecanone, 9-methyl- (9CI) (CA INDEX NAME)



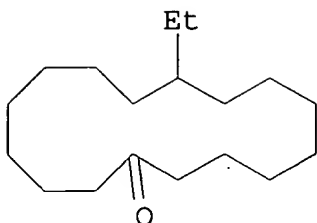
RN 398509-51-8 HCAPLUS

CN Cyclohexadecanone, 8-methyl- (9CI) (CA INDEX NAME)



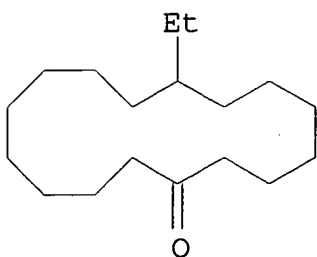
RN 398509-52-9 HCAPLUS

CN Cyclohexadecanone, 9-ethyl- (9CI) (CA INDEX NAME)



RN 398509-54-1 HCAPLUS

CN Cyclohexadecanone, 8-ethyl- (9CI) (CA INDEX NAME)

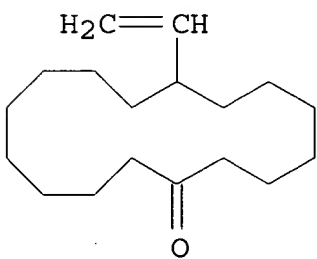


IT 398509-53-0P 398509-56-3P

(novel macrocyclic ketones as odor enhancers in perfume compns.)

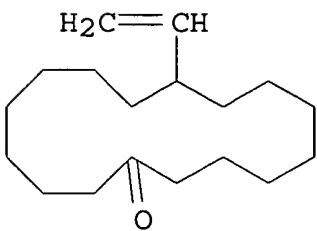
RN 398509-53-0 HCAPLUS

CN Cyclohexadecanone, 8-ethenyl- (9CI) (CA INDEX NAME)



RN 398509-56-3 HCAPLUS

CN Cyclohexadecanone, 9-ethenyl- (9CI) (CA INDEX NAME)



- IT 398509-41-6P 398509-46-1P
(novel macrocyclic ketones as odor enhancers in perfume compns.)
- IT 398509-40-5P 398509-45-0P
(novel macrocyclic ketones as odor enhancers in perfume compns.)
- IT 398509-47-2P 398509-48-3P 398509-49-4P
398509-50-7P 398509-51-8P 398509-52-9P
398509-54-1P
(novel macrocyclic ketones as odor enhancers in perfume compns.)
- IT 398509-53-0P 398509-56-3P
(novel macrocyclic ketones as odor enhancers in perfume compns.)

L25 ANSWER 2 OF 27 HCAPLUS COPYRIGHT 2003 ACS on STN
2001:381039 Document No. 135:107073 Sequenced Reactions with
Samarium(II) Iodide. Sequential Intramolecular Barbier
Cyclization/Grob Fragmentation for the Synthesis of Medium-Sized
Carbocycles. Molander, Gary A.; Le Huerou, Yvan; Brown, Giles A.
(Roy and Diana Vagelos Laboratories Department of Chemistry,
University of Pennsylvania, Philadelphia, PA, 19104-6323, USA).
Journal of Organic Chemistry, 66(13), 4511-4516 (English) 2001.
CODEN: JOCEAH. ISSN: 0022-3263. Publisher: American Chemical
Society.

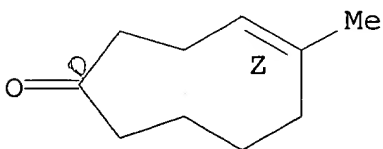
AB Samarium(II) iodide was used to access eight-, nine-, and
ten-membered carbocycles via a domino reaction composed of a
cyclization/fragmentation process. 2-(Iodoalkyl)-, 2-(iodomethyl)allyl-, and 2-(2-iodomethyl)benzyl-2-methyl-3-
(methanesulfonyloxy)cycloalkanones were subjected to Barbier-type
reductive coupling conditions. Intermediate cycloalkanedione
derivs. were also treated under similar conditions, providing
bicyclic hydroxy ketones with complete diastereoselectivity and high
yields. This method represents a general and efficient approach to
a variety of highly functionalized, stereodefined carbocycles.

IT 79310-41-1P 80533-33-1P 94089-66-4P
141600-11-5P
(prepn. of medium-sized carbocycles via intramol. Barbier-type
coupling/fragmentation mediated by samarium iodide)

RN 79310-41-1 HCAPLUS

CN 4-Cyclononen-1-one, 5-methyl-, (4Z)- (9CI) (CA INDEX NAME)

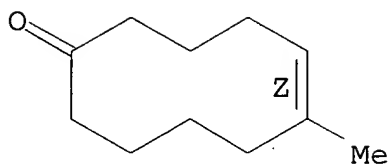
Double bond geometry as shown.



RN 80533-33-1 HCAPLUS

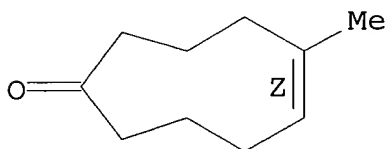
CN 5-Cyclodecen-1-one, 6-methyl-, (5Z)- (9CI) (CA INDEX NAME)

Double bond geometry as shown.

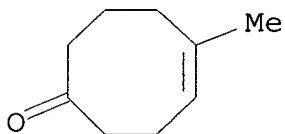


RN 94089-66-4 HCAPLUS
CN 5-Cyclononen-1-one, 5-methyl-, (5Z) - (9CI) (CA INDEX NAME)

Double bond geometry as shown.



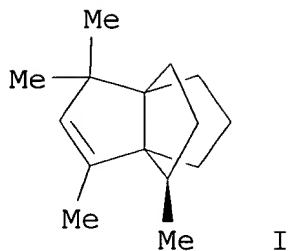
RN 141600-11-5 HCAPLUS
CN 4-Cycloocten-1-one, 5-methyl- (9CI) (CA INDEX NAME)



IT 79310-41-1P 80533-33-1P 94089-66-4P
141600-11-5P
(prepn. of medium-sized carbocycles via intramol. Barbier-type
coupling/fragmentation mediated by samarium iodide)

L25 ANSWER 3 OF 27 HCAPLUS COPYRIGHT 2003 ACS on STN
1998:606859 Document No. 129:302726 .alpha.-Ketenyl radical
intermediates in the synthesis of propellanes. A formal synthesis of
modhephene. De Boeck, Benoit; Pattenden, Gerald (Department of
Chemistry, Nottingham University, Nottingham, NG7 2RD, UK).
Tetrahedron Letters, 39(38), 6975-6978 (English) 1998. CODEN:
TELEAY. ISSN: 0040-4039. OTHER SOURCES: CASREACT 129:302726.
Publisher: Elsevier Science Ltd..

GI



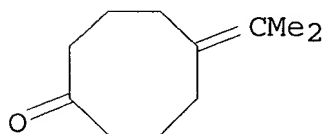
AB A tandem transannulation - cyclization sequence from a cyclooctenyl substituted .alpha.-ketenyl radical intermediate is used as the basis of a new, formal, synthesis of the naturally occurring triquinane modhephene (I).

IT 214467-11-5P

(.alpha.-ketenyl radical intermediates in synthesis of propellanes, formal synthesis of modhephene)

RN 214467-11-5 HCAPLUS

CN Cyclooctanone, 5-(1-methylethylidene)- (9CI) (CA INDEX NAME)



IT 214467-11-5P

(.alpha.-ketenyl radical intermediates in synthesis of propellanes, formal synthesis of modhephene)

L25 ANSWER 4 OF 27 HCAPLUS COPYRIGHT 2003 ACS on STN

1995:560784 Document No. 123:257068 Photoinduced molecular transformations. Part 155. General synthesis of macrocyclic ketones based on a ring expansion involving a selective .beta.-scission of alkoxy radicals, its application to a new synthesis of (.+-.)-isocaryophyllene and (.+-.)-caryophyllene, and a conformational analysis of the two sesquiterpenes and the radical intermediate in the synthesis by MM3 calculations. [Erratum to document cited in CA123:33403]. Suginome, Hiroshi; Kondoh, Takahiko; Gogonea, Camelia; Singh, Vishwakarma; Goto, Hitoshi; Osawa, Eiji (Org. Synthesis Div., Faculty Engineering, Hokkaido Univ., Sapporo, 060, Japan). Journal of the Chemical Society, Perkin Transactions 1: Organic and Bio-Organic Chemistry (9), 1200 (English) 1995. CODEN: JCPRB4. ISSN: 0300-922X. Publisher: Royal Society of Chemistry.

AB The errors were not reflected in the abstr. or the index entries.

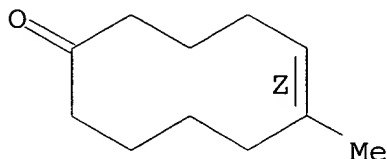
IT 80533-33-1P 80540-33-6P

(prepn. of caryophyllene via macrocyclic ketone formation by .beta.-scission of alkoxy radicals (Erratum))

RN 80533-33-1 HCAPLUS

CN 5-Cyclodecen-1-one, 6-methyl-, (5Z) - (9CI) (CA INDEX NAME)

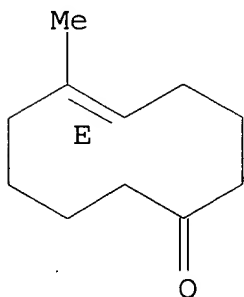
Double bond geometry as shown.



RN 80540-33-6 HCAPLUS

CN 5-Cyclodecen-1-one, 6-methyl-, (E) - (9CI) (CA INDEX NAME)

Double bond geometry as shown.



IT 80533-33-1P 80540-33-6P

(prepn. of caryophyllene via macrocyclic ketone formation by
.beta.-scission of alkoxy radicals (Erratum))

L25 ANSWER 5 OF 27 HCAPLUS COPYRIGHT 2003 ACS on STN

1995:439799 Document No. 123:198308 Diquinanes, eight-membered carbocycles and new di-bridged bis-.pi.-allyl complexes by intramol. reactions of unsaturated tricarbonyl [trimethylenemethane]iron complexes. Non destructive ozonolysis of trimethylenemethane complexes. Franck-Neumann, Michel; Kastler, Andre (Inst. Chim., Univ. Pasteur, Strasbourg, F-67008, Fr.). Synlett (1), 61-3 (English) 1995. CODEN: SYNLES. ISSN: 0936-5214. OTHER SOURCES: CASREACT 123:198308. Publisher: Thieme.

AB Tricarbonyl[TMM]iron complexes bearing an olefinic side chain were oxidized by Me₃NO in boiling benzene. When the TMM and the reactive C:C bond are sepd. by 3C-spacers, novel dibridged dicarbonyl [bis-.pi.-allyl]iron complexes, as well as methylenediquinanes or 5-vinylcyclooctenones were obtained selectively, depending on the substitution pattern and the configuration of the starting TMM complexes. Their synthesis was achieved via cross conjugated tricarbonyl[pentadienyl]iron cations and by use of the unprecedented ozonolysis of mixts. of TMM and diene complexes with homoallylic side chains to [TMM]Fe(CO)₃ aldehydes, which resulted in a chem.

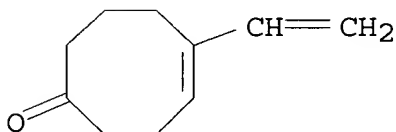
purifn. by selective destruction of the diene complexes.

IT 164468-46-6P 164468-47-7P

(prepn. of diquinanes, eight-membered carbocycles, and new di-bridged bis-allyl complexes by intramol. reaction of unsatd. [trimethylenemethane]iron complexes via destructive ozonolysis)

RN 164468-46-6 HCAPLUS

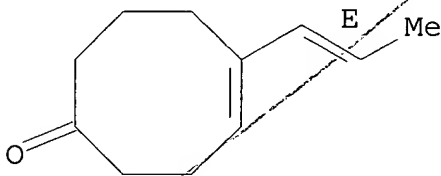
CN 4-Cycloocten-1-one, 5-ethenyl- (9CI) (CA INDEX NAME)



RN 164468-47-7 HCAPLUS

CN 4-Cycloocten-1-one, 5-(1-propenyl)-, (E)- (9CI) (CA INDEX NAME)

Double bond geometry as shown.



IT 164468-46-6P 164468-47-7P

(prepn. of diquinanes, eight-membered carbocycles, and new di-bridged bis-allyl complexes by intramol. reaction of unsatd. [trimethylenemethane]iron complexes via destructive ozonolysis)

L25 ANSWER 6 OF 27 HCAPLUS COPYRIGHT 2003 ACS on STN

1995:317209 Document No. 123:33403 Photoinduced molecular transformations. Part 155. General synthesis of macrocyclic ketones based on a ring expansion involving a selective .beta.-scission of alkoxy radicals, its application to a new synthesis of (.+-.)-isocaryophyllene and (.+-.)-caryophyllene, and a conformational analysis of the two sesquiterpenes and the radical intermediate in the synthesis by MM3 calculations. Sugimoto, Hiroshi; Kondoh, Takahiko; Gogonea, Camelia; Singh, Vishwakarma; Goto, Hitoshi; Osawa, Eiji (Org. Synthesis Div., Faculty Engineering, Hokkaido Univ., Sapporo, 060, Japan). Journal of the Chemical Society, Perkin Transactions 1: Organic and Bio-Organic Chemistry (1), 69-81 (English) 1995. CODEN: JCPRB4. ISSN: 0300-922X. Publisher: Royal Society of Chemistry.

AB The method used for a general synthesis of macrocyclic ketones based on a ring expansion involving a selective .beta.-scission of alkoxy radicals was extended and modified. Thus, cycloalkanones were transformed into .alpha.-(.omega.-iodoalkyl)cycloalkanones by alkylation of lithium enolates with either 1,3-diiodopropane or

1,4-diiodobutane. Treatment of these .alpha.-iodoalkyl cyclic ketones with samarium iodide gave bicyclic tertiary alcs. The generation of the alkoxy radicals from the bicyclic alcs. by irradiation of their hypoiodites generated with mercury(II) oxide-iodine-pyridine in benzene resulted in a selective .beta.-scission of their ring-junction bond to give high yields of macrocyclic ketones carrying an iodine which can be removed with tributyltin hydride. The method was then applied to new syntheses of (.+-.)-isocaryophyllene and (.+-.)-caryophyllene. The populations of conformers of caryophyllene, isocaryophyllene, and several related compounds, including a radical intermediate in the synthesis, were calculated by the empirical force-field method. The relative populations of conformers comprising the radical intermediate generated by .beta.-scission of the ring-junction bond of the alkoxy radicals derived from cis-transoid-cis-4,4,8-trimethyltricyclo[6.3.0.0^{2,5}]undecan-1-ol mentioned above were correlated with the three products.

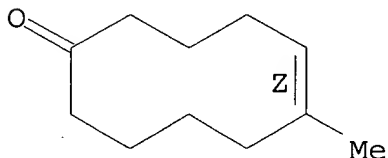
IT 80533-33-1P 80540-33-6P

(prepn. of caryophyllene via macrocyclic ketone formation by .beta.-scission of alkoxy radicals)

RN 80533-33-1 HCAPLUS

CN 5-Cyclodecen-1-one, 6-methyl-, (5Z)- (9CI) (CA INDEX NAME)

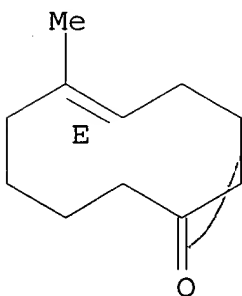
Double bond geometry as shown.



RN 80540-33-6 HCAPLUS

CN 5-Cyclodecen-1-one, 6-methyl-, (E)- (9CI) (CA INDEX NAME)

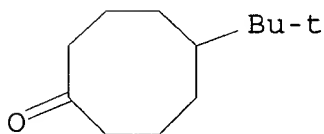
Double bond geometry as shown.



IT 80533-33-1P 80540-33-6P

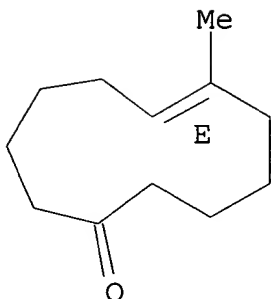
(prepn. of caryophyllene via macrocyclic ketone formation by .beta.-scission of alkoxy radicals)

- L25 ANSWER 7 OF 27 HCAPLUS COPYRIGHT 2003 ACS on STN
1995:296317 Document No. 123:55068 Selective homologation of ketones and aldehydes with diazoalkanes promoted by organoaluminum reagents. Maruoka, Keiji; Concepcion, Arnel B.; Yamamoto, Hisashi (Sch. Eng., Nagoya Univ., Nagoya, 464-01, Japan). Synthesis (Spec. Issue), 1283-90 (English) 1994. CODEN: SYNTBF. ISSN: 0039-7881. Publisher: Thieme.
- AB Organoaluminum-promoted single homologation or ring expansion of ketones and aldehydes with diazoalkanes has been described, and among various organoaluminum reagents, exceptionally bulky methylaluminum bis(2,6-di-tert-butyl-4-methylphenoxide) (MAD) is found to be highly effective for the selective homologation of various ketones and aldehydes.
- IT 15753-46-5P
(selective homologation of ketones and aldehydes with diazoalkanes promoted by organoaluminum reagents)
- RN 15753-46-5 HCAPLUS
CN Cyclooctanone, 5-(1,1-dimethylethyl)- (9CI) (CA INDEX NAME)



- IT 15753-46-5P
(selective homologation of ketones and aldehydes with diazoalkanes promoted by organoaluminum reagents)
- L25 ANSWER 8 OF 27 HCAPLUS COPYRIGHT 2003 ACS on STN
1992:407548 Document No. 117:7548 Carbocyclic ring expansion reactions via free radical pathways. Part III. Baldwin, Jack E.; Adlington, Robert M.; Singh, Rajinder (Dyson Perrins Lab., Univ. Oxford, Oxford, OX1 3QY, UK). Tetrahedron, 48(16), 3385-412 (English) 1992. CODEN: TETRAB. ISSN: 0040-4020.
- AB The free radical ring expansion methodol. recently described (J.E. Baldwin et al., 1988, 1989, 1991), leading to medium-ring ketones from cyclohexanone precursors, has been applied to different side chains and ring sizes. In addn., precursors based on lactone rings have been prepd. and subjected to radical-forming reaction conditions.
- IT 141884-46-0P
(prepn. of)
- RN 141884-46-0 HCAPLUS
CN 6-Cycloundecen-1-one, 6-methyl-, (E)- (9CI) (CA INDEX NAME)

Double bond geometry as shown.



IT 141884-46-0P
(prepn. of)

L25 ANSWER 9 OF 27 HCAPLUS COPYRIGHT 2003 ACS on STN
1992:255482 Document No. 116:255482 Preparation of oxabicycloalkane
ethers and related compounds as herbicides. Schlecht, Matthew Fred
(du Pont de Nemours, E. I., and Co., USA). PCT Int. Appl. WO
9203440 A1 19920305, 297 pp. DESIGNATED STATES: W: AU, CA, JP, US;
RW: AT, BE, CH, DE, DK, ES, FR, GB, GR, IT, LU, NL, SE. (English).
CODEN: PIXXD2. APPLICATION: WO 1991-US5438 19910806. PRIORITY: US
1990-568487 19900816.

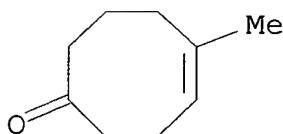
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* STRUCTURE DIAGRAM TOO LARGE FOR DISPLAY - AVAILABLE VIA OFFLINE PRINT *

AB The title compds. [I-V; X = C1-6 alkoxy, PhCH₂O, halo, OR₅, NR₆R₇,
etc.; R₁ = H, (deuterated) C1-3 alkyl; R₂ = H, C1-4 alkyl; R₃ = H,
C2-4 alkenyl, C2-4 alkynyl, (un)substituted C1-3 alkyl; R₂R₃ = 5- or
6-membered spiro- or fused ring; R₄ = H, C1-3 alkyl, C2-4 alkenyl,
C1-6 acyl, benzoyl; R₅ = H, (un)substituted C1-3 alkyl;
(un)substituted Ph, etc.; R₆, R₇ = H, C1-3 alkyl; R₆R₇ = 5- or
6-membered (un)substituted (un)satd. N-, O, or S-contg.
heterocyclyl; Q = CH₂W, benzo-fused residue Q₁; R₈ = H, halo, C1-3
alkyl, OR₉, SR₉, cyano; R₉ = C1-3 (halo)alkyl; J = CH₂, NR₁₀, O, S,
a double bond with the adjacent C; R₁₀ = H, C1-3 alkyl; W =
(un)substituted Ph, 5 to 7-membered (un)substituted heterocyclyl;
q₁, q₂ = 0-2, with a proviso] were prepd. Swern oxidn. of
cis-cyclooctane-1,5-diol gave 92% cyclooctane-1,5-dione which was
methylated-epoxidized (66%) by MeLi, and the resulting
5-methyl-9-oxabicyclo[3.3.1]nonan-1-ol dehydrated by refluxing with
2-naphthalenesulfonic acid in C₆H₆ to give 97% 5-methylcyclooct-4-
en-1-one. This was ketalized (82%) by HOCH₂CH₂OH, the ketal
oxidized (68%) by Me₃NO.2H₂O in the presence of OsO₄, and the
resulting dioxaspirododecadiol deriv. monobenzylated to give 95%
title compd. VI. The latter at 400 g/ha preemergence gave almost
complete control of barnyard grass with no damage to barley and

little damage to rice and wheat.

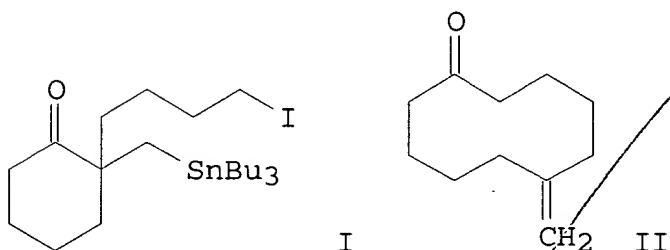
IT 141600-11-5P, 5-Methylcyclooct-4-en-1-one
(prepn. and ketalization of, by ethylene glycol, in prepn. of herbicides)
RN 141600-11-5 HCAPLUS
CN 4-Cycloocten-1-one, 5-methyl- (9CI) (CA INDEX NAME)



IT 141600-11-5P, 5-Methylcyclooct-4-en-1-one
(prepn. and ketalization of, by ethylene glycol, in prepn. of herbicides)

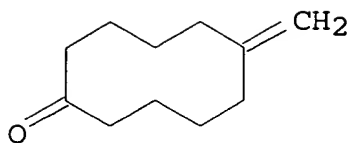
L25 ANSWER 10 OF 27 HCAPLUS COPYRIGHT 2003 ACS on STN
1991:655667 Document No. 115:255667 Carboxyclic ring expansion reactions via radical chain processes. Part II. Baldwin, Jack E.; Adlington, Robert M.; Robertson, Jeremy (Dyson Perrins Lab., Univ. Oxford, Oxford, OX1 3QY, UK). Tetrahedron, 47(33), 6795-812 (English) 1991. CODEN: TETRAB. ISSN: 0040-4020. OTHER SOURCES: CASREACT 115:255667.

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AB The further exploitation of the homolytic ring expansion reaction of cyclohexanone derivs. is described. The application of this methodol. to the prepn. of exomethylene cycloalkanones, .alpha.-alkylated cyclodecanones, indanones, and decalinols is described. Thus, treating cyclohexanone I with AIBN and Bu₃SnH gave 77% methylenecyclodecanone II.

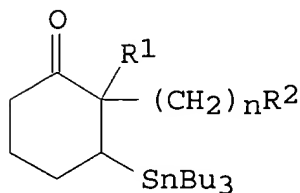
IT 70185-12-5P
(prepn. of)
RN 70185-12-5 HCAPLUS
CN Cyclodecanone, 6-methylene- (9CI) (CA INDEX NAME)



IT 70185-12-5P
(prepn. of)

L25 ANSWER 11 OF 27 HCAPLUS COPYRIGHT 2003 ACS on STN
1989:496700 Document No. 111:96700 Carbocyclic ring expansion
reactions via radical chain processes. Baldwin, Jack E.; Adlington,
Robert M.; Robertson, Jeremy (Dyson Perrins Lab., Univ. Oxford,
Oxford, OX1 3QY, UK). Tetrahedron, 45(4), 909-22 (English) 1989.
CODEN: TETRAB. ISSN: 0040-4020. OTHER SOURCES: CASREACT 111:96700.

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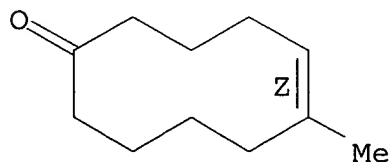
AB Cyclohexanones I ($R_1 = H, D, Me, CO_2Me$; $n = 3, 4$; $R_2 = \text{iodo}, \text{SePh}$)
were treated with Bu_3SnH and azobisisobutyronitrile to give
cyclononenones and cyclodecenones.

IT 80533-33-1P 80540-33-6P 87362-57-0P
94089-66-4P 94089-67-5P
(prepn. of)

RN 80533-33-1 HCAPLUS

CN 5-Cyclodecen-1-one, 6-methyl-, (5Z) - (9CI) (CA INDEX NAME)

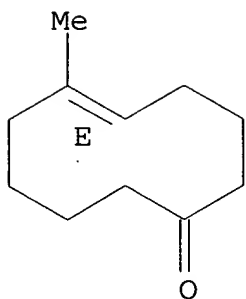
Double bond geometry as shown.



RN 80540-33-6 HCAPLUS

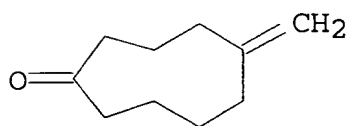
CN 5-Cyclodecen-1-one, 6-methyl-, (E) - (9CI) (CA INDEX NAME)

Double bond geometry as shown.



RN 87362-57-0 HCAPLUS

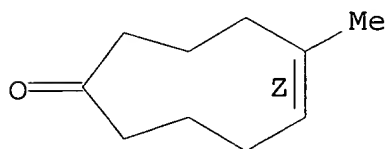
CN Cyclononanone, 5-methylene- (9CI) (CA INDEX NAME)



RN 94089-66-4 HCAPLUS

CN 5-Cyclononen-1-one, 5-methyl-, (5Z)- (9CI) (CA INDEX NAME)

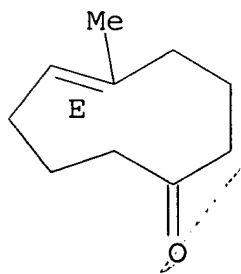
Double bond geometry as shown.



RN 94089-67-5 HCAPLUS

CN 5-Cyclononen-1-one, 5-methyl-, (E)- (9CI) (CA INDEX NAME)

Double bond geometry as described by E or Z.



IT 80533-33-1P 80540-33-6P 87362-57-0P

94089-66-4P 94089-67-5P

(prepn. of)

L25 ANSWER 12 OF 27 HCAPLUS COPYRIGHT 2003 ACS on STN
1989:212184 Document No. 110:212184 1,5-Disubstituted
cyclooctatetraenes. Lyttle, Matthew H.; Streitwieser, Andrew;
Miller, Michael J. (Dep. Chem., Univ. California, Berkeley, CA,
94720, USA). Journal of Organic Chemistry, 54(10), 2331-5 (English)
1989. CODEN: JOCEAH. ISSN: 0022-3263. OTHER SOURCES: CASREACT
110:212184.

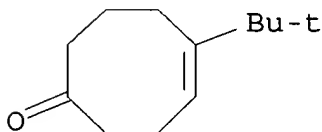
AB 1,5-Di-tert-butylcyclooctatetraene (I) and 1,5-
diphenylcyclooctatetraene (II) were prepd. from 1,5-cyclooctadiene
in 10 steps and in 11% and 1% overall yield, resp. An alternative
route gave II in 10% overall yield in eight steps, but this route
was not effective for I. Both pathways share a common appropriately
substituted intermediate, 5-phenyl-9-oxobicyclo[3.3.1]nonan-1-ol,
and 5-tert-butyl-9-oxabicyclo[3.3.1]nonan-1-ol.
1,1',5,5'-Tetra-tert-butyluranocene, prepd. from I, was stable to
water and substantially insensitive to air.

IT 119770-14-8P

(prepn. and phenylselenylation of)

RN 119770-14-8 HCAPLUS

CN 4-Cycloocten-1-one, 5-(1,1-dimethylethyl)- (9CI) (CA INDEX NAME)

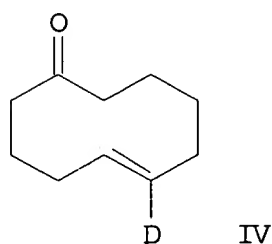
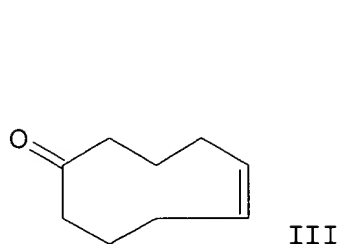
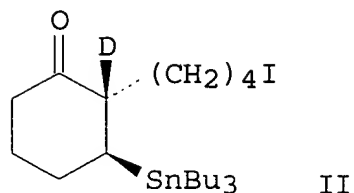
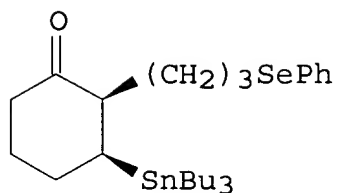


IT 119770-14-8P

(prepn. and phenylselenylation of)

L25 ANSWER 13 OF 27 HCAPLUS COPYRIGHT 2003 ACS on STN
1989:212181 Document No. 110:212181 Carbocyclic ring expansion
reactions via radical chain processes. Baldwin, Jack E.; Adlington,
Robert M.; Robertson, Jeremy (Dyson Perrins Lab., Univ. Oxford,
Oxford, OX1 3QY, UK). Journal of the Chemical Society, Chemical
Communications (21), 1404-6 (English) 1988. CODEN: JCCCAT. ISSN:
0022-4936. OTHER SOURCES: CASREACT 110:212181.

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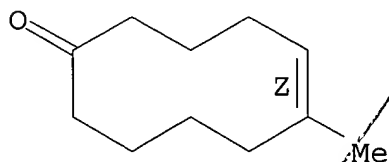
AB Treating cis- and trans-.alpha.-alkyl-.beta.-stannylcyclohexanones, e.g., I and II, resp., with Bu₃SnH and AIBN in C₆H₆ gave cis- and trans-cyclononones and -cyclodecenones, III and IV. The stereochem. of the cyclohexanones detcs. the stereochem. of the ring-expanded products.

IT 80533-33-1P 80540-33-6P 87362-57-0P
94089-66-4P 94089-67-5P
(prepn. of)

RN 80533-33-1 HCAPLUS

CN 5-Cyclodecen-1-one, 6-methyl-, (5Z) - (9CI) (CA INDEX NAME)

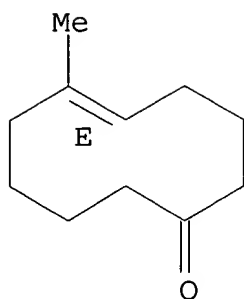
Double bond geometry as shown.



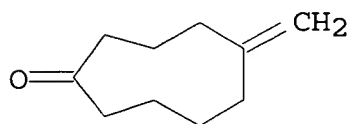
RN 80540-33-6 HCAPLUS

CN 5-Cyclodecen-1-one, 6-methyl-, (E) - (9CI) (CA INDEX NAME)

Double bond geometry as shown.

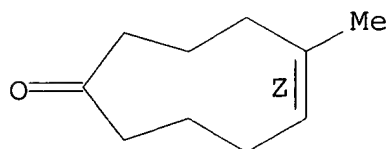


RN 87362-57-0 HCAPLUS
CN Cyclononanone, 5-methylene- (9CI) (CA INDEX NAME)



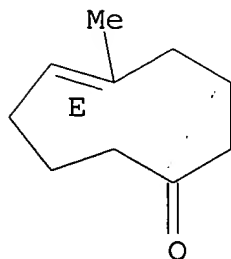
RN 94089-66-4 HCAPLUS
CN 5-Cyclononen-1-one, 5-methyl-, (5Z)- (9CI) (CA INDEX NAME)

Double bond geometry as shown.



RN 94089-67-5 HCAPLUS
CN 5-Cyclononen-1-one, 5-methyl-, (E)- (9CI) (CA INDEX NAME)

Double bond geometry as described by E or Z.

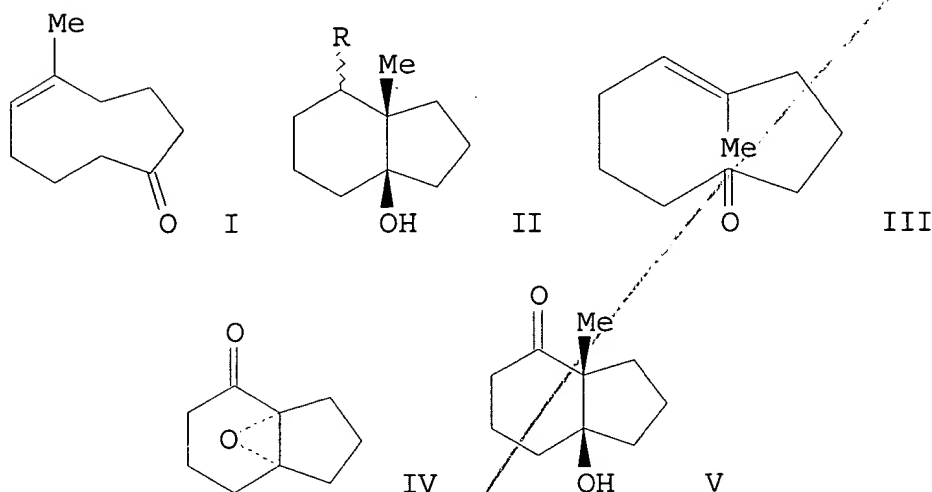


IT 80533-33-1P 80540-33-6P 87362-57-0P
94089-66-4P 94089-67-5P

(prepn. of)

L25 ANSWER 14 OF 27 HCAPLUS COPYRIGHT 2003 ACS on STN
 1985:61839 Document No. 102:61839 Wharton fragmentation of
 monosulfonates of methylhexahydroindandiolis. Caine, Drury;
 McCloskey, Candice J.; Van Derveer, Donald (Sch. Chem., Georgia
 Inst. Technol., Atlanta, GA, 30332, USA). Journal of Organic
 Chemistry, 50(2), 175-9 (English) 1985. CODEN: JOCEAH. ISSN:
 0022-3263. OTHER SOURCES: CASREACT 102:61839.

GI

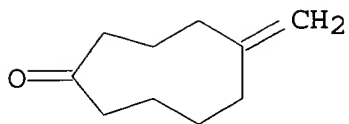


AB (Z)-5-Methylcyclo-non-5-en-1-one (I) was obtained by treatment of an
 85:15 mixt. of 4.alpha.- (II, R = .alpha.-tosyloxy) and
 4.beta.- (tosyloxy)hexahydroindan II (R = .beta.-tosyloxy) with
 KOCMe₃ in Me₃COH. The corresponding E isomer (III) was also
 produced in a small quantity in this expt. and in reasonable yield
 when mesylate II (R = .beta.-MeSO₂O) was treated under similar
 conditions. However, III was not isolated in pure form. The
 hexahydroindandiolis that were used to prep. the monosulfonates were
 obtained by redn. of epoxyindanone IV with Li and NH₃(l) followed by
 addn. of MeI to give cis-hydroxyhexahydroindanone V and then redn.
 of the carbonyl group in V with metal hydrides or Li in NH₃(l). The
 crystal structure of V 2,4-dinitrophenylhydrazone was detd.

IT 87362-57-0P 94089-66-4P 94089-67-5P
 (prepn. of)

RN 87362-57-0 HCAPLUS

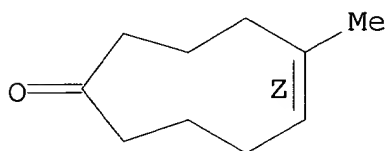
CN Cyclo-nonanone, 5-methylene- (9CI) (CA INDEX NAME)



RN 94089-66-4 HCAPLUS

CN 5-Cyclononen-1-one, 5-methyl-, (5Z) - (9CI) (CA INDEX NAME)

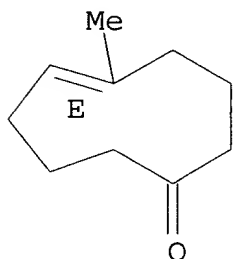
Double bond geometry as shown.



RN 94089-67-5 HCAPLUS

CN 5-Cyclononen-1-one, 5-methyl-, (E) - (9CI) (CA INDEX NAME)

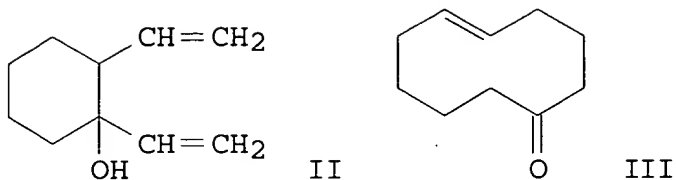
Double bond geometry as described by E or Z.



IT 87362-57-0P 94089-66-4P 94089-67-5P
(prepn. of)

L25 ANSWER 15 OF 27 HCAPLUS COPYRIGHT 2003 ACS on STN
1985:24150 Document No. 102:24150 Oxy-Cope rearrangement assisted by
mercuric trifluoroacetate in stoichiometric and catalytic
quantities. Bluthé, Norbert; Malacria, Max; Gore, Jacques (Lab.
Chim. Org., Univ. Claude Bernard Lyon I, Villeurbanne, 69622, Fr.).
Tetrahedron, 40(17), 3277-84 (French) 1984. CODEN: TETRAB. ISSN:
0040-4020. OTHER SOURCES: CASREACT 102:24150.

GI



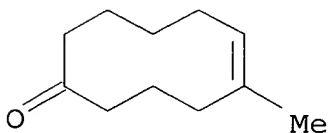
AB Tertiary 1,5-hexadien-3-ols are transformed at room temp. into .delta.-ethylenic ketones in 35-90% yields by treatment with one molar equiv. $\text{Hg}(\text{O}_2\text{CCF}_3)_2$ (I) followed by demercuration of the intermediate .alpha.-mercuro ketone with NaBH_4 or by treatment with 0.2 molar equiv. of I in the presence of one molar equiv. LiO_2CCF_3 or $\text{F}_3\text{CSO}_3\text{Li}$. The reactions are highly stereoselective, the E isomer of the ketone forming 80-95% of the product. The highest selectivity was obsd. under the second conditions. Thus, treating alc. II with I for 2 h at room temp. gave 50% cyclodecenone III.

IT 84292-10-4P 86173-54-8P 92286-92-5P
93916-12-2P 93916-14-4P

(prepn. of)

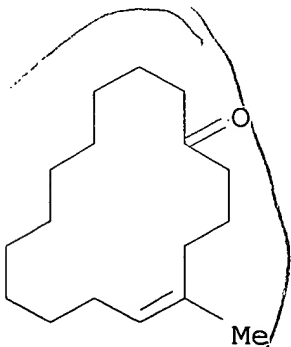
RN 84292-10-4 HCAPLUS

CN 5-Cyclodecen-1-one, 5-methyl- (9CI) (CA INDEX NAME)



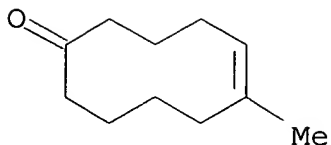
RN 86173-54-8 HCAPLUS

CN 5-Cyclohexadecen-1-one, 5-methyl- (9CI) (CA INDEX NAME)



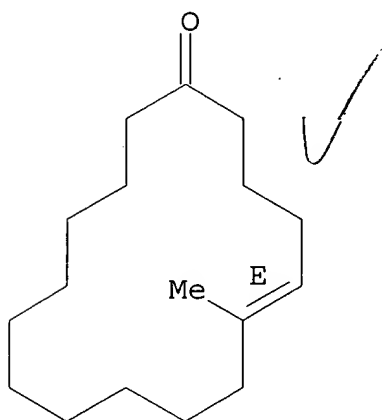
RN 92286-92-5 HCAPLUS

CN 5-Cyclodecen-1-one, 6-methyl- (7CI, 9CI) (CA INDEX NAME)



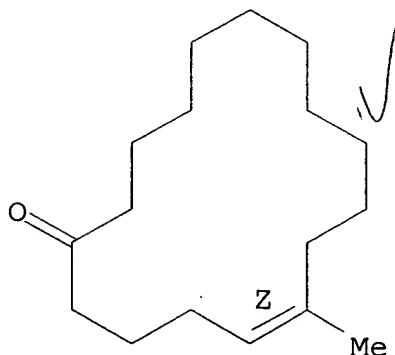
RN 93916-12-2 HCAPLUS
 CN 5-Cyclohexadecen-1-one, 6-methyl-, (E)- (9CI) (CA INDEX NAME)

Double bond geometry as shown.



RN 93916-14-4 HCAPLUS
 CN 5-Cyclohexadecen-1-one, 6-methyl-, (Z)- (9CI) (CA INDEX NAME)

Double bond geometry as shown.



IT 84292-10-4P 86173-54-8P 92286-92-5P
 93916-12-2P 93916-14-4P
 (prepn. of)

6,6-dimethylcycloundecanone and its silicon and germanium derivatives, using dipole moments and proton NMR (250 MHz).. Mazerolles, Pierre; Faucher, Alfreda; Mauret, Pierre; Fayet, Jean Pierre; Mermillod-Blardet, Danielle (Lab. Organomet., Univ. Paul Sabatier, Toulouse, 31062, Fr.). Journal de Chimie Physique et de Physico-Chimie Biologique, 80(6), 553-7 (French) 1983. CODEN: JCPBAN. ISSN: 0021-7689.

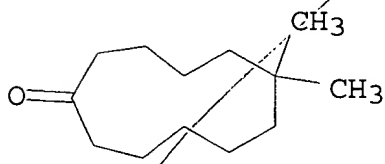
AB The conformations of 6,6-dimethyl-6-sila- (and 6-germa)cycloundecanones and of the corresponding cycloalkanones were studied, using 250 MHz NMR and dipole moment measurements in soln. at 25.degree.. The synthesis of 6,6-dimethylcycloundecanone was carried out in seven steps, starting from dimethylglutaric acid. The nature of the heteroatom has no noticeable influence on the conformational equil.

IT 89131-64-6P

(prepn. and conformation of)

RN 89131-64-6 HCAPLUS

CN Cycloundecanone, 6,6-dimethyl- (9CI) (CA INDEX NAME)

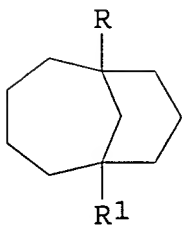


IT 89131-64-6P

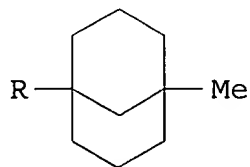
(prepn. and conformation of)

L25 ANSWER 17 OF 27 HCAPLUS COPYRIGHT 2003 ACS on STN 1983:557879 Document No. 99:157879 Palladium-catalyzed cyclization of 1,5-bis(methylene)cyclooctane. Application to one carbon ring enlargement. Heumann, A.; Reglier, M.; Waegell, B. (Cent. Saint-Jerome, Univ. Aix-Marseille III, Marseille, 13397, Fr.). Tetrahedron Letters, 24(19), 1971-4 (English) 1983. CODEN: TELEAY. ISSN: 0040-4039.

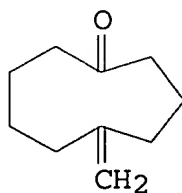
GI



II



III



IV

AB Treating 1,5-bis(methylene)cyclooctane (I) with PdR₂-CuR₁₂ (R, R₁ = Cl, OAc) and LiCl at 25.degree. gave 75-83% bicyclodecane II and

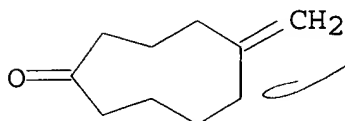
.1toreq.6% bicyclononane III, while treating I with CuCl₂ at 70.degree. gave 95% III. Treating II (R = Cl, R₁ = OAc) with Me₃COK gave cyclononanone IV.

IT 87362-57-0P

(prepn. of, from bismethylenecyclooctane)

RN 87362-57-0 HCAPLUS

CN Cyclononanone, 5-methylene- (9CI) (CA INDEX NAME)



IT 87362-57-0P

(prepn. of, from bismethylenecyclooctane)

L25 ANSWER 18 OF 27 HCAPLUS COPYRIGHT 2003 ACS on STN

1983:453067 Document No. 99:53067 Oxy-Cope rearrangement at ambient temperature catalyzed by bis(benzonitrile)palladium dichloride. Bluthé, Norbert; Malacria, Max; Gore, Jacques (Lab. Chim. Org. I, Univ. Claude Bernard Lyon I, Villeurbanne, 96922, Fr.). Tetrahedron Letters, 24(11), 1157-60 (French) 1983. CODEN: TELEAY. ISSN: 0040-4039. OTHER SOURCES: CASREACT 99:53067.

AB 5-Substituted 1,5-hexadien-3-ols isomerized to .delta.-ethylenic ketones at room temp. in the presence of catalytic amts. of [PhCN]₂PdCl₂ (I). E.g., isomerization of CH₂:CHCMe(OH)CH₂CMe:CH₂ in THF contg. 0.1 equiv I for 3 h gave CH₂:CMe(CH₂)₃COME, quant.

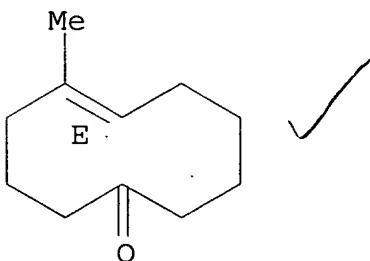
IT 86530-85-0P 86530-86-1P 86530-87-2P

(prepn. of)

RN 86530-85-0 HCAPLUS

CN 5-Cyclodecen-1-one, 5-methyl-, (E)- (9CI) (CA INDEX NAME)

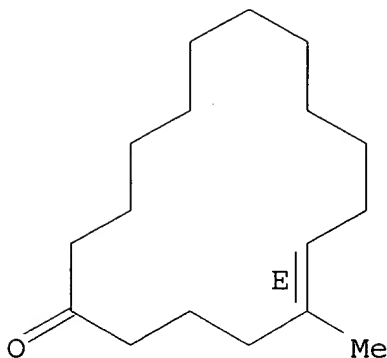
Double bond geometry as shown.



RN 86530-86-1 HCAPLUS

CN 5-Cyclodecen-1-one, 5-methyl-, (E)- (9CI) (CA INDEX NAME)

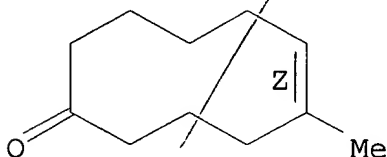
Double bond geometry as shown.



RN 86530-87-2 HCAPLUS

CN 5-Cyclodecen-1-one, 5-methyl-, (Z)- (9CI) (CA INDEX NAME)

Double bond geometry as shown.



IT 86530-85-0P 86530-86-1P 86530-87-2P
(prepn. of)

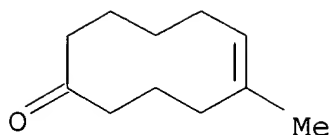
L25 ANSWER 19 OF 27 HCAPLUS COPYRIGHT 2003 ACS on STN
1983:421957 Document No. 99:21957 .delta.-Ethylenic carbonyl
compounds. Bluthe, Norbert; Gore, Jacques; Malacria, Max
(Rhone-Poulenc Sante, Fr.). Eur. Pat. Appl. EP 69010 A1 19830105,
11 pp. DESIGNATED STATES: R: AT, BE, CH, DE, FR, GB, IT, LI, LU,
NL, SE. (French). CODEN: EPXXDW. APPLICATION: EP 1982-401147
19820622. PRIORITY: FR 1981-12301 19810623.

AB Dienols RCH:CR1C(OH)R2CHR3CR4:CHR5 [R, R3, and R5 (same or
different) are H, hydrocarbyl; R1 = H; R2 and R4 are the same or
different hydrocarbyl; or R2R3 = alkylene] were contacted with Pd2+
complexes to yield R2COCHR1CHRCHR5CR4:CHR3. Thus,
CH2:CHC(OH)MeCH2CMe:CH2 was treated with PdCl2(PhCN)2 in THF at
.apprx.20.degree. to give MeCOCH2CH2CH2CMe:CH2.

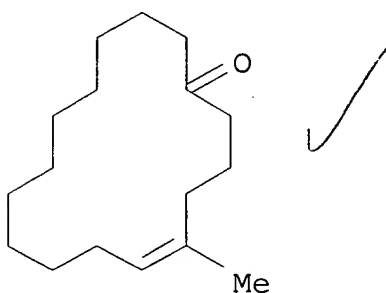
IT 84292-10-4P 86173-54-8P
(prepn. of)

RN 84292-10-4 HCAPLUS

CN 5-Cyclodecen-1-one, 5-methyl- (9CI) (CA INDEX NAME)



RN 86173-54-8 HCAPLUS
 CN 5-Cyclohexadecen-1-one, 5-methyl- (9CI) (CA INDEX NAME)

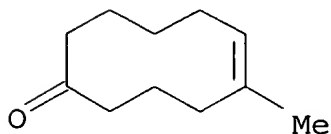


IT 84292-10-4P 86173-54-8P
 (prepn. of)

L25 ANSWER 20 OF 27 HCAPLUS COPYRIGHT 2003 ACS on STN
 1983:53179 Document No. 98:53179 .delta.-Ethylenic unsaturated
 carbonyl compounds. Bluthé, Norbert; Gore, Jacques; Malacria, Max
 (Rhône-Poulenc Santé, Fr.). Eur. Pat. Appl. EP 60767 A1 19820922,
 16 pp. DESIGNATED STATES: R: AT, BE, CH, DE, FR, GB, IT, LU, NL,
 SE. (French). CODEN: EPXXDW. APPLICATION: EP 1982-400405
 19820308. PRIORITY: FR 1981-4600 19810309; FR 1981-12300 19810623.
 AB R1CH:CR2CR(OH)CHR3CR4:CHR5 [R = acyclic hydrocarbyl contg. double or
 triple bonds; R1, R2, R3, R4, and R5 (same or different) are H,
 acyclic hydrocarbyl contg. double or triple bonds] were contacted
 with mercuric salts or mixts. of mercuric salts and Li salts at
 between -40.degree. and +80.degree. to give the resp.
 RCOCHR2CHR1CHR5CR4:CHR3. Thus, CH2:CHCMe(OH)CH2CMe:CH2 was treated
 with HgCl2 at .apprx.20.degree. to give MeCOCH2CH2CH2CMe:CH2.

IT 84292-10-4P
 (prepn. of)

RN 84292-10-4 HCAPLUS
 CN 5-Cyclodecen-1-one, 5-methyl- (9CI) (CA INDEX NAME)

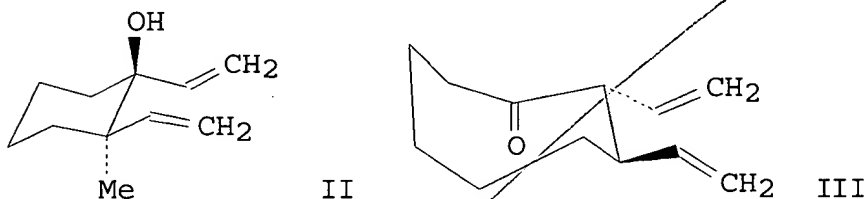


IT 84292-10-4P

(prepn. of)

L25 ANSWER 21 OF 27 HCAPLUS COPYRIGHT 2003 ACS on STN
 1982:162169 Document No. 96:162169 .alpha. Vinylation of ketones. A
 general method using (phenylseleno)acetaldehyde. Clive, Derrick L.
 J.; Russell, Charles G.; Suri, Suresh Chander (Dep. Chem., Univ.
 Alberta, Edmonton, AB, T6G 2G2, Can.). Journal of Organic
 Chemistry, 47(9), 1632-41 (English) 1982. CODEN: JOCEAH. ISSN:
 0022-3263.

GI



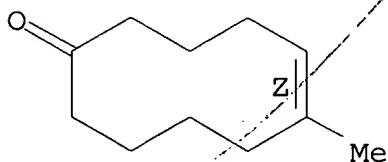
AB PhSeCH₂CHO (I) is used as a synthetic equiv. of the vinyl carbonium ion, CH₂:CH⁺. A no. of ketone enolates, usually as Zn salts, were condensed with I to give .beta.-hydroxy selenides (av. yield 78% for 10 examples). Treatment of these substances with MeSO₂Cl and Et₃N afforded the corresponding .alpha.-vinyl ketones (av. yield 72% for 10 examples). This methodol. provides access to compds. e.g., II and III, that are correctly constituted to undergo Cope and oxy-Cope rearrangements. Introduction of .alpha.-isopropenyl groups is also feasible by using (phenylseleno)acetone in the initial condensation step.

IT 80533-33-1P 80540-33-6P
 (prepn. of)

RN 80533-33-1 HCAPLUS

CN 5-Cyclodecen-1-one, 6-methyl-, (5Z) - (9CI) (CA INDEX NAME)

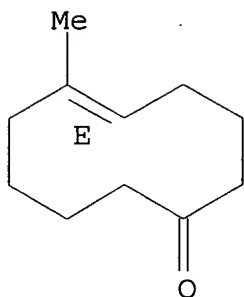
Double bond geometry as shown.



RN 80540-33-6 HCAPLUS

CN 5-Cyclodecen-1-one, 6-methyl-, (E) - (9CI) (CA INDEX NAME)

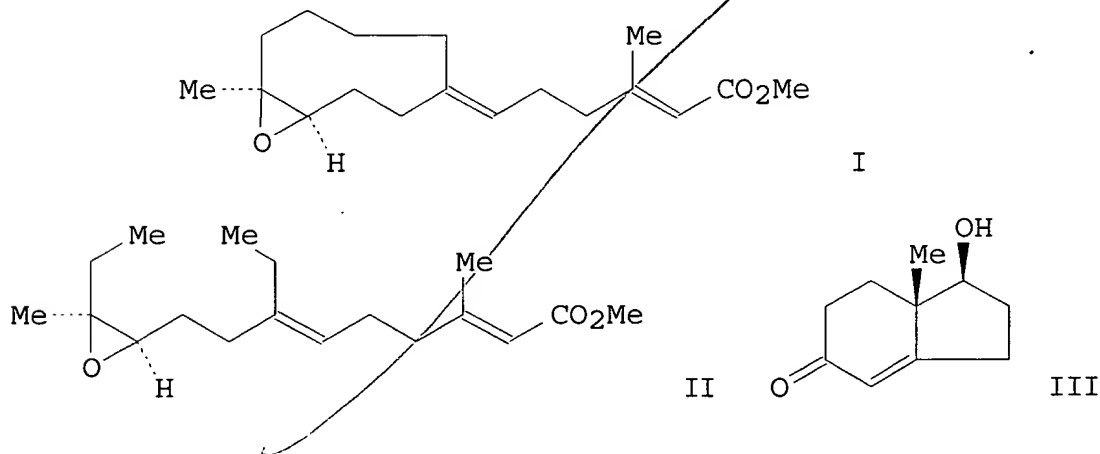
Double bond geometry as shown.



IT 80533-33-1P 80540-33-6P
(prepn. of)

L25 ANSWER 22 OF 27 HCAPLUS COPYRIGHT 2003 ACS on STN
1981:550280 Document No. 95:150280 Products active on arthropods.
III. Insect juvenile hormone mimics. Part 3. Cyclononane analog
of Cecropia juvenile hormone. Patel, Hemant A.; Dev, Sukh
(Malti-Chem Res. Cent., Vadodara, India). Tetrahedron, 37(8),
1577-81 (English) 1981. CODEN: TETRAB. ISSN: 0040-4020.

GI



AB The cyclononane analog I of the Cecropia juvenile hormone II was
prepd. in 10 steps from the bicycloketol III. I is only moderately
active against *Dysdercus cingulatus*.

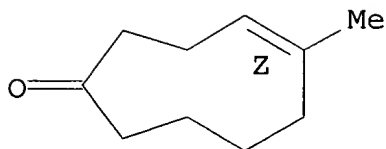
IT 79310-41-1P

(prepn. and Wittig reaction of)

RN 79310-41-1 HCAPLUS

CN 4-Cyclononen-1-one, 5-methyl-, (4Z) - (9CI) (CA INDEX NAME)

Double bond geometry as shown.



IT 79310-41-1P
(prepn. and Wittig reaction of)

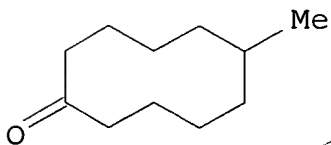
L25 ANSWER 23 OF 27 HCAPLUS COPYRIGHT 2003 ACS on STN
1981:102606 Document No. 94:102606 Dimethylcyclodecyl cations.
Evidence for μ -hydrido bridging. Kirchen, R. P.; Ranganayakulu, K.; Rauk, A.; Singh, B. P.; Sorensen, T. S. (Dep. Chem., Univ. Calgary, Calgary, AB, T2N 1N4, Can.). Journal of the American Chemical Society, 103(3), 588-96 (English) 1981. CODEN: JACSAT. ISSN: 0002-7863.

AB The carbocations, 1,5- and 1,6-dimethylcyclodecyl, are postulated to have a μ -hydrido-bridged structure. This assignment is based on the observation of a single very high-field hydrogen in the ^1H NMR, anomalously low coupling consts. involving this hydrogen, and very small isotope perturbation shifts using the Saunderson's criterion for equilibrating and resonance structural distinction. Both positional and conformational isomerization is possible in these bridged ions, but no evidence for cis-trans isomerization was found. The μ -hydrido bridging is best treated as an open three-center, two-electron resonance system involving a single potential min. for the bridged hydrogen. The bridging hydrogen is not electrophilic, and the bridged ions cannot be prepd. by protonating the central bond of decalins nor can the μ -hydrogen be removed as a proton. Numerous theor. calcns. were performed and correlated with the exptl. data.

IT 76393-81-2P 76393-87-8P
(prepn. of)

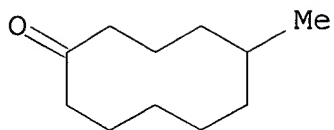
RN 76393-81-2 HCAPLUS

CN Cyclodecanone, 6-methyl- (6CI, 7CI, 9CI) (CA INDEX NAME)



RN 76393-87-8 HCAPLUS

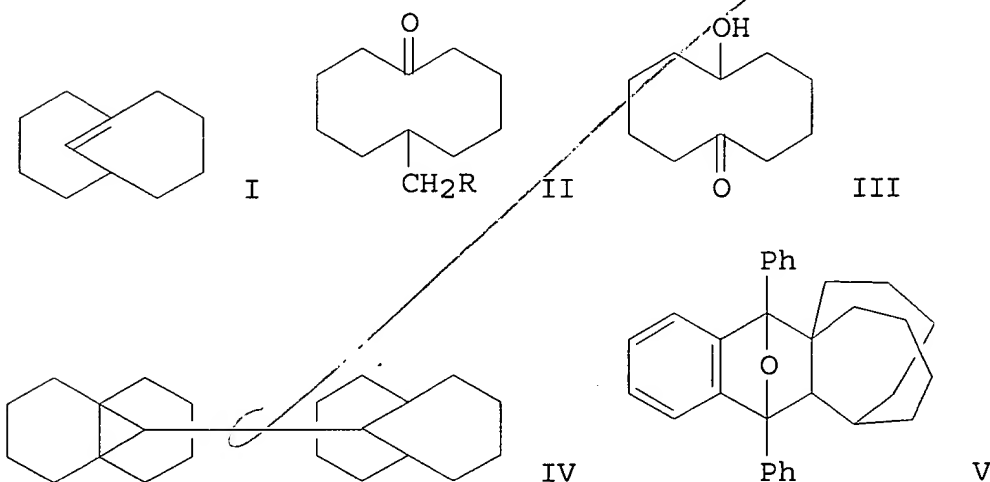
CN Cyclodecanone, 5-methyl- (9CI) (CA INDEX NAME)



IT 76393-81-2P 76393-87-8P
(prepn. of)

L25 ANSWER 24 OF 27 HCAPLUS COPYRIGHT 2003 ACS on STN
1979:203536 Document No. 90:203536 Synthesis and dimerization of
bicyclo[4.4.1]undec-1(11)-ene, a bridged trans-cycloheptene.
Becker, Konrad B.; Chappuis, Jacques L. (Inst. Org. Chem., Univ.
Basel, Basel, Switz.). Helvetica Chimica Acta, 62(1), 34-43
(English) 1979. CODEN: HCACAV. ISSN: 0018-019X.

GI

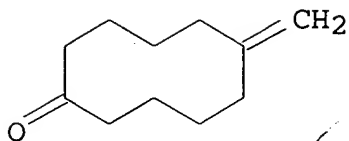


AB The Bredt olefin I was prepd. by intramol. Wittig reaction of
phosphonium bromide II (R = P⁺Ph₃Br⁻) which was prepd. in 6 steps
from cyclodecanone III via II (R = OH). I could not be isolated,
but dimerized rapidly to cyclopropane compd. IV. I was trapped in
situ by 2,5-diphenylbenzo[c]furan to give 2:1 Diels-Alder adducts
endo- and exo-V.

IT 70185-12-5P
(prepn. and attempted hydrogen bromide addn. to)

RN 70185-12-5 HCAPLUS

CN Cyclodecanone, 6-methylene- (9CI) (CA INDEX NAME)



IT 70185-12-5P

(prepn. and attempted hydrogen bromide addn. to)

L25 ANSWER 25 OF 27 HCAPLUS COPYRIGHT 2003 ACS on STN

1977:4508 Document No. 86:4508 Formation of monohomocyclooctatetraene dianions in liquid ammonia. Analysis of the nucleophilic reactivity of the cyclononatrienyl anions generated upon solvent protonation. Paquette, Leo A.; Ley, Steven V.; Traynor, Sean G.; Martin, Jeffrey T.; Geckle, J. M. (Evans Chem. Lab., Ohio State Univ., Columbus, OH, USA). Journal of the American Chemical Society, 98(25), 8162-72. (English) 1976. CODEN: JACSAT. ISSN: 0002-7863.

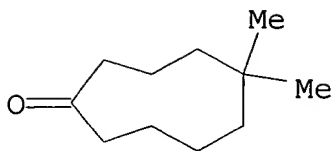
AB Reactions of the cyclononatrienyl anion (I) and its 8-methyl (II) and 8,8-dimethyl (III) homologs, which are generated via in situ protonation by solvent NH₃ of homocyclooctatetraene dianions, proceed at C-3 and C-5, which are the sites of highest electron d. (1H NMR anal.). Methanol quenching studies at -70.degree. show that II is attacked by a proton preferably at C-3 (ratio 3:1), whereas III undergoes preferential attack at C-5 (by a factor of 7). However, methylation of III predominates at C-3 (1.97:1). The alkylation of II introduces the added feature of stereoselectivity. The 3:1 preference for protonation at C-3 is reduced during methylation to approx. 1:1. Alkylation at C-3 proceeds with high stereoselectivity (8:1) for the trans isomer; bonding of the Me group to C-5 is almost statistical from the cis and trans directions. Crossover in regioselectivity operates in the two reaction types opposite to the 8,8-dimethyl example. Structural assignments in all instances were made on the basis of catalytic hydrogenation, independent unequivocal synthesis of the resulting cyclononane deriv., and suitable application of 13C NMR spectroscopy. The results are interpreted in terms of the exothermicity of the specific reaction and the degree of bonding accessibility available in the various low-energy conformations of the carbanions as they experience sp² .fwdarw. sp³ rehybridization. By variable temp. 1H and 13C NMR studies of certain all-cis-1,3,6-cyclononatriene products, it is possible to assess those conformational factors and differing steric strains which gain importance in these cyclic polyolefins.

IT 61265-62-1P

(prepn. and Wittig reaction of)

RN 61265-62-1 HCAPLUS

CN Cyclononanone, 5,5-dimethyl- (9CI) (CA INDEX NAME)



IT 61265-62-1P
(prepn. and Wittig reaction of)

L25 ANSWER 26 OF 27 HCAPLUS COPYRIGHT 2003 ACS on STN
1975:442899 Document No. 83:42899 Synthesis of disubstituted derivatives of bicyclo[3.3.1]nonane. Baklan, V. F. (Inst. Org. Khim., Kiev, USSR). Zhurnal Organicheskoi Khimii, 11(4), 746-50 (Russian) 1975. CODEN: ZORKAE. ISSN: 0514-7492.

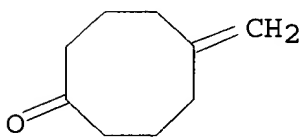
GI For diagram(s), see printed CA Issue.

AB Desulfurization of I over Raney-Ni gave 91% diester (II, R = Me, R1 = CO2Me) which was hydrolyzed to yield 12.3% acid (II, R = H, R1 = CO2H) and 44.9% monoester (II, R = Me, R1 = CO2H). Electrolysis of the latter two in MeOH gave 69.7% II (R = Me, R1 = OMe) which was brominated with 63% HBr to give 95% II (R = H, R1 = Br). The latter was converted to 90% amide (III) which was rearranged by NaOBr-MeOH to give 90.2% carbamate (IV). Boiling the carbamate with 10% aq. NaOH gave 79% cyclooctanone (V, X = O) which in a Wittig reaction gave 32.3% 1,5-dimethylenecyclooctane (V, X = CH2).

IT 56031-31-3P
(prepn. and Wittig reaction of)

RN 56031-31-3 HCAPLUS

CN Cyclooctanone, 5-methylene- (9CI) (CA INDEX NAME)



IT 56031-31-3P
(prepn. and Wittig reaction of)

L25 ANSWER 27 OF 27 HCAPLUS COPYRIGHT 2003 ACS on STN
1972:487969 Document No. 77:87969 Acid-catalyzed isomerization of bicyclo[6.1.0]nonanes functionally substituted at position 4. Gras, J. L.; Bertrand, M. (Fac. Sci., Marseilles, Fr.). Bulletin de la Societe Chimique de France (5), 2024-7 (French) 1972. CODEN: BSCFAS. ISSN: 0037-8968.

GI For diagram(s), see printed CA Issue.

AB Bicyclo[6.1.0]nonan-4-one (I) was isomerized with Et2O.BF3 to hydrindanone (II) and cyclooctenone (III) and the 4-hydroxy analog of I was isomerized to bicyclic ethers (IV and V, R = H) and a cyclooctanone (VI, R = H). 4-Deuteriobicyclo[6.1.0]nonan-4-ol was

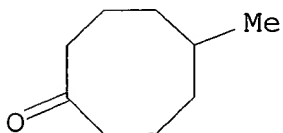
isomerized to IV (R = D), V (R = D), and VI (R = D). Mechanisms of the isomerizations, including a transannular hydride migration, were discussed.

IT 38451-99-9P 38452-03-8P

(prepn. of)

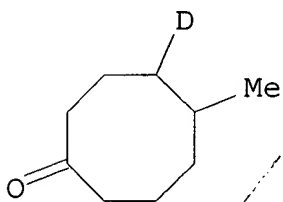
RN 38451-99-9 HCAPLUS

CN Cyclooctanone, 5-methyl- (7CI, 9CI) (CA INDEX NAME)



RN 38452-03-8 HCAPLUS

CN Cyclooctanone-4-d, 5-methyl- (9CI) (CA INDEX NAME)



IT 38451-99-9P 38452-03-8P

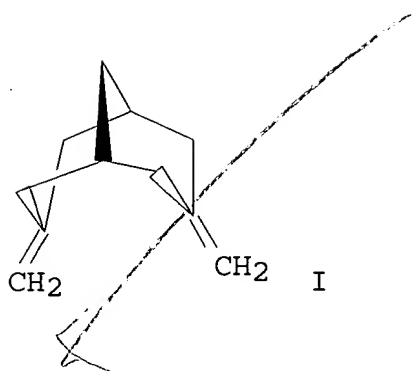
(prepn. of)

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L28 ANSWER 1 OF 15 HCAPLUS COPYRIGHT 2003 ACS on STN

1999:309834 Document No. 131:87519 Transannular interaction in bifunctional olefins and ketones: a semiempirical electron density analysis. Chow, Tahsin J.; Li, Lih-Pyng (Institute of Chemistry, Academia Sinica, Taipei, Taiwan, Peop. Rep. China). Tetrahedron, 55(19), 6067-6074 (English) 1999. CODEN: TETRAB. ISSN: 0040-4020. Publisher: Elsevier Science Ltd..

GI



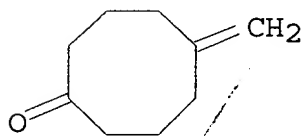
AB Electron densities on the olefinic carbons of some dimethylene compds. are calcd. by semiempirical model PM3, and the values are compared with those of the corresponding monomethylene compds. A relation is obsd. between the change of electron d. .DELTA.(C) and the change of ^{13}C NMR chem. shift .DELTA..delta.. A correlation is also found between .DELTA.(C) and .DELTA.(O), i.e. the C and O atoms, of methylene-ketones. The electron d. differences are induced by 3 types of transannular interactions: electrostatic force, orbital interactions through bond (TB) and orbital interactions through space (TS). Electrostatic force is the most prominent factor for ketones in which the high polarity of carbonyl group can apply a strong field effect onto nearby atoms. For nonpolar methylene groups, orbital interactions can be transmitted either TS or TB more effectively than electrostatic force. A conformational anal., performed on a dimethylene compd. I, confirms the existence of TS interaction between the double bonds.

IT 56031-31-3

(semiempirical electron d. anal. of transannular interaction in bifunctional olefins and ketones)

RN 56031-31-3 HCAPLUS

CN Cyclooctanone, 5-methylene- (9CI) (CA INDEX NAME)



IT 56031-31-3

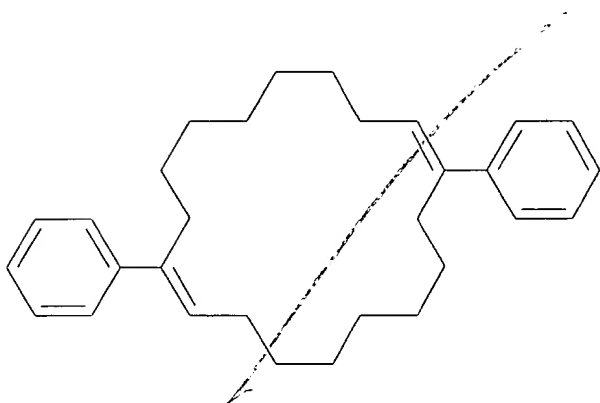
(semiempirical electron d. anal. of transannular interaction in bifunctional olefins and ketones)

L28 ANSWER 2 OF 15 HCAPLUS COPYRIGHT 2003 ACS on STN

1996:26658 Document No. 124:201339 Reactions of Molecules with Two Equivalent Functional Groups. 5. Anomalous Reactivity of 1,10-Cyclooctadecanedione. Crystal and Molecular Structures of cis,cis-1,10-Diphenyl-1,10-cyclooctadiene and the Stereoisomers of 1,10-Diphenyl-1,10-cyclooctadecanediol. Macomber, Roger S.; Constantinides, Ioannis; Bauer, Jeanette Krause; Smith, Gregory;

Button, Angela; Lindstrom, David O. (Department of Chemistry, University of Cincinnati, Cincinnati, OH, 45221-0172, USA). Journal of Organic Chemistry, 61(2), 727-34 (English) 1996. CODEN: JOCEAH. ISSN: 0022-3263. Publisher: American Chemical Society.

GI



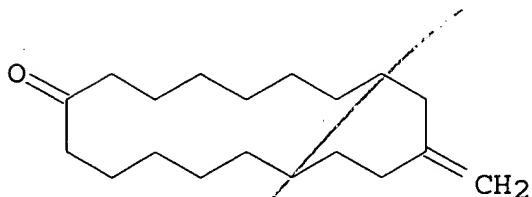
AB The reaction of the 1,10-cyclooctadecanedione (3) with Ph Grignard produces (with rate const. k_1) the conjugate base (6-M) of 10-hydroxy-10-phenylcyclooctadecanone (6), which is subsequently converted (with rate const. k_2) to the conjugate base of the title diol, as a mixt. of the cis (7, 55%) and trans (8, 45%) isomers. The ratio k_2/k_1 , 2.2 ± 0.4 , indicates that the carbonyl group in 6-M is 4.4 times as reactive as each carbonyl in 3. Competition expts. further demonstrate that the relative rates (per carbonyl) for addn. of phenylmagnesium bromide to 3, 10-methylenecyclooctadecanone (11), and cyclopentadecanone (12) are 1.0:1.92:0.60. Possible reasons for this order of reactivity are discussed. Diols 7 and 8 undergo facile double dehydration to form the title diene cis,cis-I, which is predicted by mol. mechanics calcs. to be the most stable of the four possible sym. diene isomers. The structures of 7, 8, and cis,cis-13 were secured by single-crystal x-ray studies.

IT 99605-57-9

(competitive reactant; Grignard reaction of cyclooctadecanedione)

RN 99605-57-9 HCAPLUS

CN Cyclooctadecanone, 10-methylene- (9CI) (CA INDEX NAME)



(competitive reactant; Grignard reaction of cyclooctadecanedione)

L28 ANSWER 3 OF 15 HCAPLUS COPYRIGHT 2003 ACS on STN

1991:489815 Document No. 115:89815 Origin of musk fragrance activity: the electron-topologic approach. Bersuker, I. B.; Dimoglo, A. S.; Gorbachov, M. Yu.; Vlad, P. F.; Pesaro, M. (Inst. Chem., Kishinev, 277028, USSR). New Journal of Chemistry, 15(5), 307-20 (English) 1991. CODEN: NJCHE5. ISSN: 0398-9836.

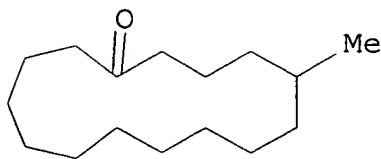
AB Based on the electron-topol. approach to the QSAR problem worked out earlier by some of the authors, the rules of musk fragrance activity are revealed and discussed in detail. It is shown that the mol. feature responsible for the musk odor can be represented by an appropriate electron-topol. matrix that includes 2 independent mol. fragments with special electronic and topol. characteristics. The 1st consist of a polar group (CO, NO, CN) whose electroneg. atom is situated sym. and at a distance of 6.7 .ANG. with respect to 2 Me (or methylene) groups, the distance between them being 2.5 .ANG.. The 2nd fragment includes 2 other Me (or methylene) groups situated at a distance of 5.5 .ANG. from each other. These 2 features are necessary conditions for musk odor, the sufficient ones including mainly the requirement that there are no bulky substituents close to the functional group making the latter sterically inaccessible. There are 362 org. compds. from different classes including macrocycles, nitrobenzene, indane, and hydronaphthalene derivs. that are analyzed in view of the musk revealed in this work, and only a few of them (7 active compds. and 8 inactive ones) apparently don't obey these rules; the Bayes probability of prediction of musk odor with these rules is $P = 0.96$. The origin of the discrepancies between the musk rules and exptl. data are discussed, and a hypothesis of dimers activity is suggested.

IT 135522-51-9

(musk fragrance activity of, mol. structure in relation to)

RN 135522-51-9 HCAPLUS

CN Cyclopentadecanone, 5-methyl- (9CI) (CA INDEX NAME)



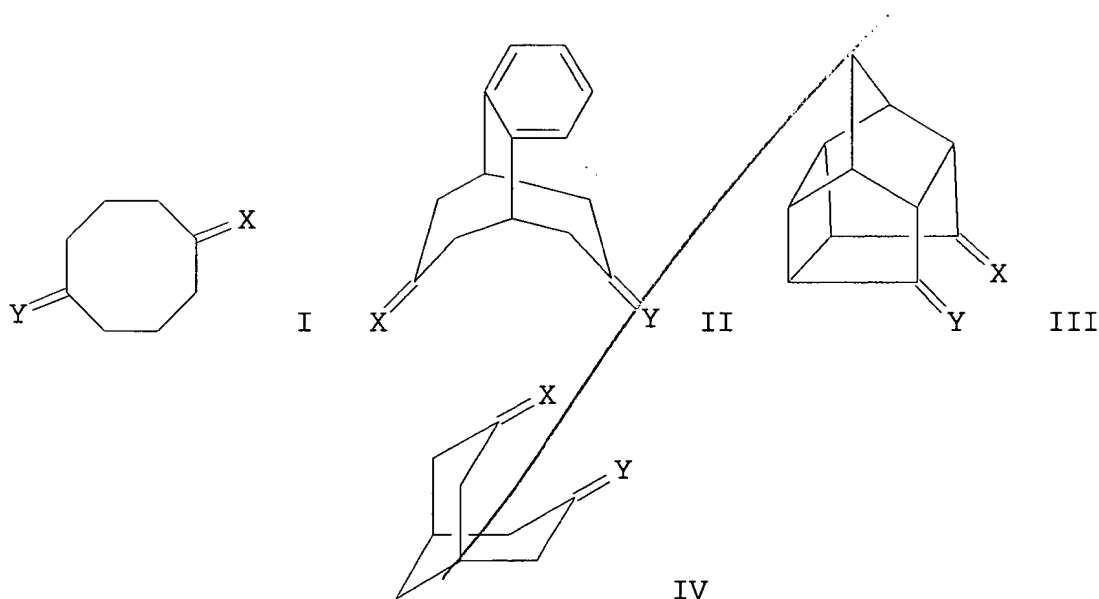
IT 135522-51-9

(musk fragrance activity of, mol. structure in relation to)

L28 ANSWER 4 OF 15 HCAPLUS COPYRIGHT 2003 ACS on STN

1984:454405 Document No. 101:54405 Carbon-13 NMR shifts as a measure of transannular interaction in unsaturated alicyclic systems. Bishop, Roger (Sch. Chem., Univ. New South Wales, Kensington, 2033, Australia). Australian Journal of Chemistry, 37(2), 319-25 (English) 1984. CODEN: AJCHAS. ISSN: 0004-9425.

GI



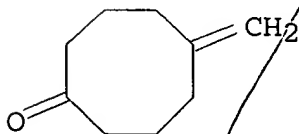
AB The ^{13}C NMR of the sp^2 atoms in the cyclooctanes I ($\text{X} = \text{Y} = \text{CH}_2, \text{O}$; $\text{X} = \text{CH}_2, \text{Y} = \text{H}_2$; $\text{X} = \text{O}, \text{Y} = \text{H}_2, \text{CH}_2$), the corresponding benzobicyclo[3.3.2] decanes II, and the corresponding 1,2,4-ethanylidene-1H-cyclobuta[cd]pentalenes III show transannular π -electron delocalizations involving the CH_2 and $\text{C}:\text{O}$ π -electrons. This study, together with that for the corresponding bicyclononanes IV (Senda, et al., 1981), shows that this is a general and reliable procedure for the detn. of transannular interactions with the potential to predict intramol. cyclizations.

IT 56031-31-3

(carbon-13 NMR of, transannular interaction in relation to)

RN 56031-31-3 HCAPLUS

CN Cyclooctanone, 5-methylene- (9CI) (CA INDEX NAME)



IT 56031-31-3

(carbon-13 NMR of, transannular interaction in relation to)

1982:67971 Document No. 96:67971 Ring size and positional constraints for μ -hydrido-bridging in dimethylcycloalkyl cations ($n = 6-9$). Kirchen, R. P.; Ranganayakulu, K.; Singh, B. P.; Sorensen, T. S. (Dep. Chem., Univ. Calgary, Calgary, AB, T2N 1N4, Can.). Canadian Journal of Chemistry, 59(14), 2173-8 (English) 1981. CODEN: CJCHAG. ISSN: 0008-4042.

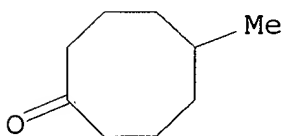
AB The in situ prepn. and NMR characterization of selected 1,n-dimethylcycloalkyl cations is reported. Both the 1,5-dimethylcyclononyl (I) and the 1,5-dimethylcyclooctyl (II) cations are assigned a μ -hydrido-bridged structure. The corresponding 1,4-dimethylcyclooctyl, 1,4-dimethylcycloheptyl, and 1,4-dimethylcyclohexyl cations are normal unbridged tertiary cations. I rearranges in part to the 1-methyl-5-ethylcyclooctyl cation which is also μ -hydrido-bridged and this rearrangement is followed by noting the disappearance of the δ -5.8 μ -H peak of the former and the appearance of a δ -6.4 μ -H peak for the latter. II is the most thermally stable μ -hydrido-bridged cation yet prepd. and possesses a chair-twist boat (TB) conformation which is frozen-out in the NMR spectrum at -120.degree.. At higher temps. one gets a chair-TB/TB-chair equilibration, ΔG thermod. = 30 kJ mol⁻¹ from NMR line broadening.

IT 38451-99-9 80926-31-4

(Grignard reaction of, with Me iodide)

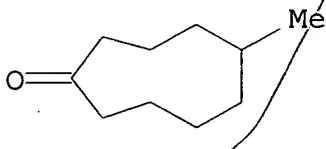
RN 38451-99-9 HCAPLUS

CN Cyclooctanone, 5-methyl- (7CI, 9CI) (CA INDEX NAME)



RN 80926-31-4 HCAPLUS

CN Cyclononanone, 5-methyl- (6CI, 9CI) (CA INDEX NAME)



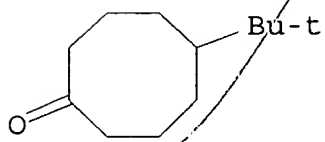
IT 38451-99-9 80926-31-4

(Grignard reaction of, with Me iodide)

L28 ANSWER 6 OF 15 HCAPLUS COPYRIGHT 2003 ACS on STN

1967:46028 Document No. 66:46028 Nuclear magnetic resonance and conformational isomerization in unsaturated cyclooctane derivatives. St. Jacques, Maurice; Brown, Mary A.; Anet, Frank A. L. (Univ. of California, Los Angeles, CA, USA). Tetrahedron Letters (47), 5947-51 (English) 1966. CODEN: TELEAY. ISSN: 0040-4039.

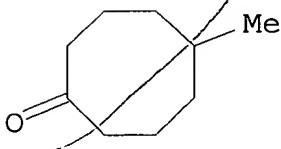
- GI For diagram(s), see printed CA Issue.
- AB cf. CA 65, 3711h. The proton N.M.R. spectra of 5,5-butylcyclooctanone (I), cyclooctanone (II), cis-cyclooctene (III), cis-cis-1,3-cyclooctadiene (IV), and cis-cis-1,5-cyclooctadiene (V) were examd. from 20 to -150.degree., I and II were dissolved in CHF₂Cl and III, IV, V in H₂C:CHCl. V did not show temp. dependent spectra but those of I-IV were illustrated. The spectrum of I at -120.degree. showed the presence of 2 Me C bands of unequal intensities and a conformation picture similar to that of tert-butylcyclooctane (VI) was assigned. Favorable conformations of I were classified into 2 distinct sets, A and B as tabulated. Interconversion, A1 .dblarw. A2 or A1 .dblarw. A3 .dblarw. A2 without "ring inversion" to a member of set B was assumed to be rapid even at -150.degree.. At temps. above -80.degree., ring inversion can take place and is responsible for the single line given by the Me₃C group. The 2 bands below -120.degree. represent mols. in sets A and B. II showed similar spectral changes with ring inversion responsible for changes observed around -120.degree.. The N.M.R. spectra of III and IV show changes at -100.degree. to -120.degree. and -85.degree. to -110.degree., presumably due to a slowing down of ring inversion, which averages the chem. shifts of the 2 CH₂ protons in III and IV. The great differences in the effects of unsatn. on the rates of ring inversion in the 6-versus the 8-membered series are very striking. The coalescence temp. is lowered from about -60.degree. to -160.degree. on going from cyclohexane to cyclohexene. By contrast, cyclooctane, cyclooctene, and cyclooctanone have similar rates of inversion.
- IT 15753-46-5
(nuclear magnetic resonance of)
- RN 15753-46-5 HCAPLUS
- CN Cyclooctanone, 5-(1,1-dimethylethyl)- (9CI) (CA INDEX NAME)



- IT 15753-46-5
(nuclear magnetic resonance of)
- L28 ANSWER 7 OF 15 HCAPLUS COPYRIGHT 2003 ACS on STN
- 1964:2797 Document No. 60:2797 Original Reference No. 60:419a-d
Diketone condensation of cyclohexanone with homologs of formaldehyde. III. Tilichenko, M. N. Uchenye Zapiski Rostovskogo-na-Donu Gosudarstvennogo Universiteta, 75, 60-5 (Unavailable) 1962. CODEN: URDGAY. ISSN: 0376-2688.
- GI For diagram(s), see printed CA Issue.
- AB Cyclohexanone was condensed with CH₂O, AcH, EtCHO, or PrCHO in the presence of alkali to yield after diln. of the reaction mixt. with H₂O an oil and crystals which were sepd. and resp. fractionally

vacuum distd. and recystd. The products were: from CH₂O, methylenedicyclohexanone, m. 61.5.degree. b1.5 147-53.degree., d₂₀ 1.0666, n_{20D} 1.5055 (dioxime, m. 171-3.degree.) and 2,3-tetramethylene-3-hydroxybicyclo[3.3.1]nonan-9-one (I), m. 166-8.degree. (oxime m. 159-61.degree.); from MeCHO, ethylidenedicyclohexanone, b. 166-7.degree. (in vacuo), d₂₀ 1.0740, n_{20D} 1.5184, (dioxime m. 164-7.degree.), and 4-methyl-2,3-tetramethylene-3-hydroxybicyclo[3.3.1]nonan-9-one, m. 15860.degree. (oxime m. 152-5.degree.); from EtCHO, propylidenedicyclohexanone, b1 168-72.degree., d₂₀ 1.0602, n_{20D} 1.5150, and 4-ethyl-2,3-tetramethyl-3-hydroxybicyclo [3.3.1]nonan-9-one, m. 161-4.degree. (oxime m. 128-30.degree.); from PrCHO, butylidenedicyclohexanone, b1.5 173-4.degree., d₂₀ 1.0549, n_{20D} 1.5118, and 4-propyl-2,3-tetramethylene-3-hydroxybicyclo[3.3.1]nonan-9-one, m. 170-3.degree. (oxime m. 112-16.degree.). The alkylidenedicyclohexanones were easily cyclized by alkali in alc. soln. forming the resp. 4-alkyl-2,3-tetramethylene-3hydroxybicyclo[3.3.1]nonan-9-ones but the reaction was reversed at elevated temps. When heated at 60.degree. with HOAc-concd. HCl or when boiled in C₆H₆ soln. with a small amt. of concd. H₂SO₄ I lost a mol. of H₂O to form an unsatd. bicyclic ketone.

IT 38451-99-9, Cyclooctanone, 5-methyl-
(prepn. of)
RN 38451-99-9 HCAPLUS
CN Cyclooctanone, 5-methyl- (7CI, 9CI) (CA INDEX NAME)



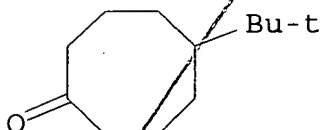
IT 38451-99-9, Cyclooctanone, 5-methyl-
(prepn. of)

L28 ANSWER 8 OF 15 HCAPLUS COPYRIGHT 2003 ACS on STN
1963:435242 Document No. 59:35242 Original Reference No. 59:6270a-g
Conformational analysis. XXVI. Some stereochemical studies of the cyclooctane ring. Allinger, Norman L.; Greenberg, Seymour (Wayne State Univ., Detroit, MI). Journal of the American Chemical Society, 84(12), 2394-402 (Unavailable) 1962. CODEN: JACSAT. ISSN: 0002-7863.

GI For diagram(s), see printed CA Issue.
AB cf. CA 55, 22185h; 57, 7128f; 59, 2863b. The preferred conformations of cis- (I) and trans-5-tert-butylcyclooctanol (II) were discussed with regard to the 3 axial-like and 3 equatorial-like positions in cyclooctanes. In agreement with the assigned conformations, I p-toluenesulfonate (III) showed a greater tendency for C-1 to C-5 hydride migration than did II p-toluenesulfonate (IV). III with NaOAc in AcOH gave 1 part 5-tert-butylcyclooctene (V) to 4 parts 1-tert-butylcyclooctene (VI). With IV, the ratio was

2 V to 1 VI. V and VI were stable under the reaction conditions. The rates of sapon. of the acid phthalates of cyclooctanol (VII), I, and II were similar and decreased in the order listed. Rates of chromic acid oxidn. in 75% AcOH decreased in the order: I, II, VII. Nuclear magnetic resonance signals for the proton attached to the O-bearing C atom in the acid phthalates of VII, I, II, cis-, and trans-4-tert-butylcyclohexanol were at 4.80, 4.92, 4.60, 4.85, and 5.09 .tau. (relative to Me₄Si), resp., indicating that nuclear magnetic resonance may be useful in solving conformational problems in cyclooctanes. The energy difference for the axial and equatorial acid phthalates was calcd. to be 0.3 kcal./mole. The ratio of I to II equilibrated under Oppenauer conditions was 1.78. Infrared analysis indicated that LiAlH₄ redn. of 5-tert-butylcyclooctanone (VIII) gave 81% I and 19% II, while catalytic hydrogenation over Pt yielded 42% I and 58% II. (CF₃CO)₂O (25 g.) at 5-10.degree. with 2.63 ml. 90% H₂O₂ and 14.0 g. VIII gave 58% .gamma.,-tert-butyl-.epsilon.-caprolactone, b₂ 130 5.degree., m. 57.5-8.5.degree. (heptane), which (10.0 g.) with 17 ml. 38% HBr and 2 ml. concd. H₂SO₄ yielded 64% 4-tert-butyl-6-bromohexanoic acid, b_{0.2} 125-30.degree. n_{25D} 1.4842; Et ester (IX), b₈ 141-4.degree., n_{25D} 1.4674. IX (20 g.) and 5.6 g. KCN in 95% EtOH refluxed 18 hrs. gave 69% Et 4-tert-butyl-6-cyanoheptanoate, b₉ 161-4.degree. n_{25D} 1.4489, which in EtOH with H₂SO₄ gave 75% di-Et 4-tert-butylheptane-1,7-dioate (X), b₅ 134-6.degree., n_{25D} 1.4428. X with LiAlH₄ in ether gave 100% 4-tert-butyl-1,7-heptanediol, b_{0.7} 131.degree., b_{25D} 1.4657, which with HBr at 125-30.degree. yielded 91% 4-tert-butyl-1,7-dibromoheptane, b₃ 130-2.degree., n_{25D} 1.4990, converted to 75% 4-tert-butyl-1,7-dicyanoheptane (XI), b₂ 165-6.degree., n_{25D} 1.4579. XI with Li N-methylanilide gave 77% VIII, b₇ 113-15.degree. n_{25D} 1.4714; 2,4-dinitrophenylhydrazone m. 172-3.degree.; semicarbazone m. 188-9.degree.. 5-tert-Butyl-2-cyanocyclooctanone m. 97.5-8.5.degree. (ether). VIII with LiAlH₄ gave 32% I, m. 60.0-0.5.degree. (pentane at -20.degree.); p-nitrobenzoate m. 109.5-10.degree.. Treatment of III with Et₄NOAc in Me₂CO followed by sapon. gave 53% II, m. 58.5-9.5.degree.; p-nitrobenzoate m. 83.5-4.5.degree.. Oxidn. of I and II with CrO₃ yielded VIII. I with phthalic anhydride in C₅H₅N heated 17 hrs. at 90.degree. gave 85% acid phthalate, m. 88.5-9.degree. (pentane); II acid phthalate m. 121-2.degree. (etherpentane); cyclooctyl acid phthalate m. 134-5.degree.. Wolff-Kishner redn. of VIII and hydrogenation of V and VI over Pt gave tert-butylcyclooctane, n_{25D} 1.4647. VIII oxime, m. 89-90.degree., with LiAlH₄ in tetrahydrofuran yielded 81% 5-tert-butylcyclooctylamine (XII), b₇ 115-19.degree., n_{25D} 1.4859; oxalate m. 273-4.degree. (decompn., sealed tube). XII with HCO₂H and HCHO heated at 100.degree. gave 79% N,N-dimethyl deriv., b₇ 125-40.degree., n_{25D} 1.4800, which in MeOH with 30% H₂O₂ gave the N-oxide, heated to 200.degree. at 7 mm. to give 20% cis-V, b₂₀ 105-10.degree., n_{25D} 1.4735, contaminated with 1% trans-V and VI. Li (8.3 g.) with 55.6 g. tert-BuCl in pentane and 14 g. cyclooctanone gave 68% 1-tert-butyl-cyclooctanol, b₁₁ 118-20.degree. n_{25D} 1.4860, which refluxed 17 hrs. with iodine in toluene gave 66% VI, b₁₁ 88-9.degree., n_{25D} 1.4750.

IT 15753-46-5, Cyclooctanone, 5-tert-butyl-
 (prepn. of)
 RN 15753-46-5 HCAPLUS
 CN Cyclooctanone, 5-(1,1-dimethylethyl)- (9CI) (CA INDEX NAME)



IT 15753-46-5, Cyclooctanone, 5-tert-butyl-
 (prepn. of)

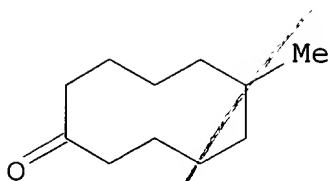
L28 ANSWER 9 OF 15 HCAPLUS COPYRIGHT 2003 ACS on STN
 1962:429422 Document No. 57:29422 Original Reference No. 57:5819a-d
 Stereospecific synthesis of 6-methyl-trans-5-cyclodecenone.
 Wharton, P. S. (Univ. of Wisconsin, Madison). Journal of Organic
 Chemistry, 26, 4781-2 (Unavailable) 1962. CODEN: JOCEAH. ISSN:
 0022-3263.

GI For diagram(s), see printed CA Issue.

AB A sequence of reactions was reported for the prepn. of trans-I, in
 which the key reaction was the facile fragmentation of II with
 concomitant formation of trans-I, the trans double bond being
 introduced stereospecifically. Treatment of III Sondheimer and Elad,
 (CA 52, 4576b) with elk. H₂O₂ yielded 8.beta.-benzoyloxy-
 9.beta.methyl-4,10.epsilon.-epoxy-3-decalone (IV), m.
 158-8.5.degree.. Addn. of N₂H₄.H₂O to IV in MeOH contg. a trace
 AcOH gave 8.beta.-benzoyloxy-9.beta.-methyl-.DELTA.3-10.epsilon.-
 octalol, m. 116-17.degree., which was subsequently hydrogenated to
 give 8.beta.-benzoyloxy-9.beta.methyl-10.epsilon.-decalol (V), m.
 119-20.degree... Without isolation of intermediate compds., V was
 successively sapond., the resulting crude diol treated with 1 equiv.
 MeSO₂Cl in pyridine, the crude monomesylate II warmed with tert-BuOK
 in tert-BuOH, and the product distd. at 0.1 mm. from a oil bath at
 100.degree. to give I, m. 18-21.degree., .lambda. (CCl₄) 5.86 .mu.;
 oxime m. 132-4.degree.. Hydrogenation of I in EtOH-AcOH with PrO₂
 followed by oximation gave 25% 6-methylcyclodecanone (VI) oxime
 (VII), m. 82-3.degree. (hexane), identical with VII prepd. from
 authentic VI Prelog and Kueng (CA 51, 3475a). VI and .lambda.
 (CF₂HCF₂CH₂OH) 227 m.mu. (.epsilon. 2750) and .lambda. (MeOH) 221
 m.mu. (.epsilon. 3050).

IT 76393-81-2, Cyclodecanone, 6-methyl-
 (prepn. of)

RN 76393-81-2 HCAPLUS
 CN Cyclodecanone, 6-methyl- (6CI, 7CI, 9CI) (CA INDEX NAME)



IT 76393-81-2, Cyclodecanone, 6-methyl-
(prepn. of)

L28 ANSWER 10 OF 15 HCAPLUS COPYRIGHT 2003 ACS on STN

1958:60938 Document No. 52:60938 Original Reference No. 52:10914b-g
Many-membered carbon rings. XVI. Acetolysis of 5,5-dimethylcyclononanol tosylate. Blomquist, A. T.; Meinwald, Yvonne C. (Cornell Univ., Ithaca, NY). Journal of the American Chemical Society, 80, 630-2 (Unavailable) 1958. CODEN: JACSAT. ISSN: 0002-7863.

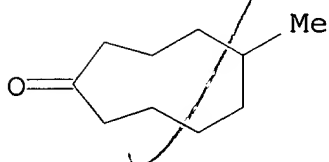
AB cf. C.A. 51, 16397b. The acetolysis of 5,5-dimethylcyclononanyl tosylate (I) has been studied with the objective of ascertaining the role of annular Me groups in medium size ring reactions. Cyclononanyl tosylate (2.96 g.), m. 43-4.degree., in 20 cc. glacial AcOH kept at 35.degree. until the acetolysis was completed, the mixt. poured into 20 cc. 10% aq. Na₂CO₃ and extd. with Et₂O, the ext. washed, dried, and evapd., and the residue chromatographed on Al₂O₃ yielded 0.43 g. cis-cyclononene, n₂₂D 1.4786, and 0.90 g. cyclononanylacetate, n₂₂D 1.4643, rate const. k₁ 8.75 .times. 10⁻⁵ sec.⁻¹ I (3.24 g.) gave in the same manner 0.7 g. olefinic products, n₂₅D 1.4743, and 1.05 g. 5,5-dimethylcyclononanyl acetate (II), n₂₅D 1.4612, rate const. k₁ 4.70 .times. 10⁻⁵ sec.⁻¹. The olefinic product (0.4141 g.) hydrogenated at 23.7.degree. and 731 mm. yielded 0.38 g. 1,1-dimethylcyclononane, n₂₅D 1.4600. 5,5-Dimethylcyclononanol (1 g.) treated 2 days at room temp. with 2 cc. Ac₂O and 4 cc. C₅H₅N gave 1.1 g. II, b_{0.3} 72.degree., n₂₅D 1.4610. CH₂:CHCO₂Me and 0.5 mole equiv. Me₂C:CH₂ heated 28 hrs. at 240.degree. di-Me .delta.-methyleneazelaate (III), b_{2.5} 124-5.degree., n₂₅D 1.4510. III (69 g.) hydrogenated in 95% EtOH over PtO₂ yielded 67.5 g. di-Me .delta.-methylazelaate (IV), b₁ 108.5-10.5.degree., n₂₅D 1.4378. IV (67.5 g.) in 140 cc. xylene added during 7.5 hrs. with stirring to 35 g. powd. Na in 2 l. refluxing xylene and 400 cc. PhMe and the mixt. worked up in the usual manner yielded 29.8 g. 1-methyl-5-oxo-6-hydroxycyclononane, b_{0.5} 75-6.degree., which reduced with 90-5% Zn dust and fractionated gave 16.7 g. 5-methylcyclononanone (V), b₁₀ 99.degree., n₂₅D 1.4714; semicarbazone, m. 167-8.degree.. V (3.02 g.) in 20 cc. dry Et₂O added slowly with stirring to 100 cc. dry Et₂O contg. MeMgI from 5.68 g. MeI and 1 g. Mg, refluxed 2 hrs., cooled, poured at 0.degree. into satd. aq. NH₄Cl, and extd. with Et₂O gave 3 g. 1,5-dimethylcyclononanol (VI), b_{1.2-1.3} 78-80.degree., n₂₅D 1.4763, needles, m. 35-48.degree.. Ketene bubbled during 1.5 hrs. into 2.79 g. VI in 10 cc. dry Et₂O with occasional cooling, washed with dil. aq. Na₂CO₃ and H₂O, dried, and evapd. gave 3 g. acetate (VII) of VI,

b0.2 62.degree., n25D 1.4607. VII (8.0 g.) dropped at the rate of 1 drop/10 sec. under N at 445-50.degree. into a vertical Pyrex tube packed with Carborundum chips, and the cold trap condensate dild. with pentane, washed, dried, and fractionated gave 1.5 g. distillate, b. 175-80.degree., n25D 1.4400, and 3.68 g. distillate, b. 200-2.degree., n25D 1.4731; the 2nd fraction redistd. gave a mixt. of olefins, b55 122-3.degree., n25D 1.4738; a 2.0077-g. portion in AcOH hydrogenated over prerduced PtO2 at 24.degree. and 736.5 mm. gave 1.8 g. 1,5-dimethylcyclononane, b50 118.degree., n25D 1.4586.

IT 80926-31-4, Cyclononanone, 5-methyl-
(prepn. of)

RN 80926-31-4 HCAPLUS

CN Cyclononanone, 5-methyl- (6CI, 9CI) (CA INDEX NAME)



IT 80926-31-4, Cyclononanone, 5-methyl-
(prepn. of)

L28 ANSWER 11 OF 15 HCAPLUS COPYRIGHT 2003 ACS on STN

1957:17023 Document No. 51:17023 Original Reference No.

51:3475g-i,3476a-d The carbon ring. LXX. Transannular displacements in the cyclodecane series. Prelog, V.; Kung, W. (Eidg. Tech. Hochschule, Zurich, Switz.). Helv. Chim. Acta, 39, 1394-406 (German) 1956.

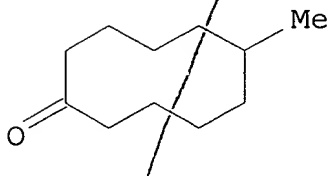
AB cf. C.A. 50, 10664b. Powd. 1-methyl-1,6-cyclodecanediol (I) (4.5 g.) treated with 150 ml. 84% H3PO4 at room temp. 4 hrs., the mixt. dild. with 3 parts H2O, extd. with pentane, the ext. dried, the pentane distd., the residue (3.9 g.) dild. with 30 ml. dry ether, 0.5 g. LiAlH4 suspended in 30 ml. ether added, the mixt. refluxed 1 hr., treated with AcOEt to decomp. the excess LiAlH4, seignette salt soln. added, the mixt. extd. with ether, the ether evapd., and the colorless, viscous liquid residue chromatographed over 120 g. Al2O3 and eluted with pentane gave 1.208 g. unstable hydrocarbon, C11H18; subsequent elution with ether yielded 2.030 g. 6-methylcyclodecanol (II). II (0.5 g.) was transformed into the p-nitrobenzoate and the salt chromatographed and fractionally crystd. gave 2 epimeric II p-nitrobenzoates: difficultly sol. white needles, m. 123-4.degree., and readily sol. white flakes, m. 64-5.degree.. II (1.2 g.) in 15 ml. pyridine added dropwise with shaking to 1 g. CrO3 in 15 ml. pyridine, the mixt. dild. with H2O, kept 24 hrs. at room temp., extd. with pentane, and the ext. washed with dil. HCl, satd. KHCO3 soln., and H2O and evapd. gave 1.3 g. crude 6-methylcyclodecanone (III); its semicarbazone, m. 202-5.degree. (decompn.) (from alc.), with 1 g. powd. o-C6H4(CO)2O distd. with H2O vapor, and the distillate extd. with pentane and distd. yielded 253 mg. III, b11

105.degree. nD20 1.4760, d23 0.9297, identified as follows: treatment with NaOEt and HCO2Et in ether, oxidation with H2O2 in alk. soln., esterification with CH2N2, and sapon. with KOH in MeOH gave a diacid identical with .delta.-methyl-sebacic acid prep'd. in a different manner. According to the proposed reaction mechanism the transformation of I into III proceeds through the formation of a tertiary carbonium ion (under the influence of the strong acid) which oxidizes the secondary HO group simultaneously with hydride displacement. To det. whether the formation of III from I proceeds through 1,6-hydride displacement, resulting in a direct carbonyl formation, or through 1,5-hydride displacement, resulting in carbonyl formation through the enol, I was oxidized with CrO3-pyridine complex to 6-hydroxy-6-methylcyclodecanone (IV), and IV reduced with LiAlD4 to 1-methyl-1,6-cyclodecanediol-6-d (V); from V with 84% H3PO4 was obtained 6-methylcyclodecanone-6-d, which would mean that 1,6-hydride displacement was occurred; if 1,5-hydride displacement occurred, 6-methylcyclodecane-6-one should be formed. No evidence was found that the transannular 1,6-hydride displacement, which proceeds very easily if the diol is of the secondary-tertiary alc. type, occurs if the diol is of the ditertiary type.

IT 76393-81-2, Cyclodecanone, 6-methyl-
(prepn. of)

RN 76393-81-2 HCAPLUS

CN Cyclodecanone, 6-methyl- (6CI, 7CI, 9CI) (CA INDEX NAME)



IT 76393-81-2, Cyclodecanone, 6-methyl-
(prepn. of)

L28 ANSWER 12 OF 15 HCAPLUS COPYRIGHT 2003 ACS on STN

1956:44332 Document No. 50:44332 Original Reference No.

50:8485d-i,8486a-i Many-membered carbon rings. XII. Stereochemical studies of some gem-dimethylcyclononane derivatives. Blomquist, A. T.; Wheeler, E. S.; Chu, Y. (Cornell Univ., Ithaca, NY). Journal of the American Chemical Society, 77, 6307-10 (Unavailable) 1955. CODEN: JACSAT. ISSN: 0002-7863.

AB The mol. flexibility of the 9-membered C ring has been investigated using 5,5-dimethylcyclononanone (I). Direct attempts to resolve I gave no indication of sepn. of stereoisomers even though well-characterized optically active derivs. were obtained. The conversion of I to 5,5-dimethylcyclonanol (II) and the resolution of the latter has been achieved. The oxidation of the optically active II afforded the inactive ketone I. It is concluded that 9-membered C rings of this type are incapable of retaining dissym. conformations at room temp. Me2C(CH2CO2H)2, b2 89-90.degree., nD20

1.4278, was prepd. in 94% yield by hypohalite oxidation of dimedon. III (200 g.) in 200 cc. dry Et₂O added as rapidly as possible with stirring to 50 g. LiAlH₄ and 1.8 l. dry Et₂O, the mixt. stirred 1 hr., dild. carefully with 200 cc. H₂O and filtered, and the combined Et₂O filtrate and washings distd. gave 110 g. Me₂C(CH₂CH₂OH)₂ (IV), b_{0.25} 95-8.degree., n_D20 1.4575. IV (264 g.) in 250 cc. glacial AcOH treated 5-6 hrs. at 130.degree. with a rapid stream of dry HBr, and the lower layer of the cooled mixt. washed with 20% aq. Na₂CO₃ and H₂O and distd. gave 350-368 g. Me₂C(CH₂CH₂Br)₂ (V), b_{1.3} 80-1.5.degree., n_D20 1.5078, d₂₀ 1.5320. IV treated with PBr₃ gave 98% V. IV treated with anhyd. HBr in the absence of AcOH gave as the main product 4,4-dimethyltetrahydropyran (VI), b. 125-7.degree. n_D20 1.4268, d₂₀ 0.8630. VI in an equal vol. glacial AcOH treated with dry HBr gave V. V (48 g.), 50 g. NaCN, 150 cc. EtOH, and 160 cc. H₂O refluxed 12 hrs. under N, most of the EtOH distd. off, the mixt. extd. with CH₂Cl₂, and the ext. distd. gave 30 g. Me₂C(CH₂CH₂CN)₂ (VII), b₇ 155-7.degree.. Crude VII (30 g.) refluxed overnight with 40 cc. each H₂O, concd. H₂SO₄, and glacial AcOH, the mixt. poured onto crushed ice, and the solid ppt. (33 g.) recrystd. from H₂O gave Me₂C(CH₂CH₂CO₂H)₂ (VIII), m. 85.5-86.degree.. Crude VIII (330 g.) esterified azeotropically with EtOH-PhMe yielded 320 g. di-Et ester (IX) of VIII, b_{0.7} 102-3.degree., n_D20 1.4394, d₂₀ 0.9854, MRD 65.4. IX (160 g.) reduced in the usual manner with 50 g. LiAlH₄ yielded 93 g. Me₂C(CH₂CH₂CH₂OH)₂ (X), b_{1.2} 128.degree., n_D20 1.4620, d₂₀ 0.9390. X (20 g.) treated in glacial AcOH with dry HBr gave 32 g. Me₂C(CH₂CH₂CH₂Br)₂ (XI). X (186 g.) treated with PBr₃ gave 309 g. XI, b₁ 96.5-98.degree., n_D20 1.5018, d₂₀ 1.4145. XI (220 g.) treated with NaCN in aq. EtOH in the usual manner gave 127 g. Me₂C(CH₂CH₂CH₂CN)₂ (XII), b_{0.9} 146.degree., n_D20 1.4540, d₂₀ 0.9200. Crude XII (from 309 g. XI) hydrolyzed yielded 230 g. Me₂C(CH₂CH₂CH₂CO₂H)₂ (XIII), m. 68.0-9.5.degree. (all m.ps. are cor.). XIII (230 g.) esterified azeotropically with EtOH-PhMe gave 248.5 g. pure di-Et ester (XIV), b_{0.05} 102.degree., n_D20 1.4412, d₂₀ 0.9562. XIV subjected to an acyloin condensation in 3:1 xylene-PhMe by the method previously described (C.A. 47, 6880c) on a 0.3-0.5-mole scale gave 6,6'-dimethylcyclononanol-2-one (XV), b_{1-1.2} 88-91.degree., n_D20 1.4845, d₂₀ 1.0177, MRD 52.0. XV (25.8 g.) reduced with 90% Zn dust and the crude product distd. gave 3 fractions: (1) b₃₅ 104-7.degree.; (2), b₃₃ 132-5.degree., n_D20 1.4718, 11.9 g.; (3), b₅ 135-7.degree.; fraction 2 converted to the semicarbazone, m. 172-3.degree., and a 21-g. portion refluxed 12 hrs. with 30 g. (CO₂H)₂ in 200 cc. H₂O, cooled, and extd. with Et₂O yielded 13.1 g. pure I, b_{8.5} 104.degree., n_D20 1.4714, n_D25 1.4696, d₂₀ 0.9389. I (36.8 g.) and 2 g. Cu(OAc)₂ added with stirring to 100 g. pure Zn dust in 194 cc. glacial AcOH, the mixt. treated during 1.5 hrs. dropwise with 250 cc. concd. HCl, refluxed 0.5 hr., cooled, dild. with H₂O, and worked up, and the product distd. gave 24.4 g. 6,6-dimethylcyclononene (XVI), b₄₀ 105-5.5.degree., n_D25 1.4716, d₂₅ 0.8531. XVI (1 g.) in 5 cc. Me₂CO treated with swirling with 60 cc. 5% aq. KMnO₄, the mixt. warmed 15 min. on a steam bath, cooled to room temp., bubbled with SO₂ until colorless, acidified, and extd. with CH₂Cl₂, and the ext. evapd. gave 400 mg. XII, m.

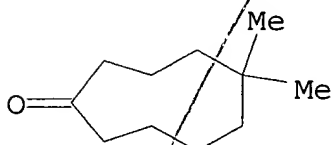
69-70.degree.. XVI (5 g.) in 20 cc. EtOH hydrogenated over 100 mg. PtO₂ yielded 3.5 g. 1,1-dimethylcyclononane, b₃₆ 104.5.degree..
(+)-.delta.-(.alpha.-Phenylethyl) semicarbazide HCl salt (XVII) (2.16 g.) and 1.62 g. NaOAc.3H₂O in 10 cc. MeOH and 5 cc. H₂O added to 3.36 g. I in 10 cc. MeOH, the mixt. kept at 50.degree., gradually cooled to room temp., and refrigerated 5 days, and the solid deposit (1.2 g.) recrystd. from abs. EtOH or hexane yielded
(+)-.delta.-(.alpha.-phenylethyl)semicarbazone (XVIII) of I, m. 107.5-9.5.degree., [.alpha.]D -52.7 .+-. 0.8.degree. (c 5, abs. EtOH); the mother liquors gave 3 addnl. crops; the mother liquor evapd., the oily residue dissolved in Et₂O and washed with H₂O, the soln. dried and evapd., the residue chromatographed on Al₂O₃, and the column eluted with pentane gave 1 g. inactive I; semicarbazone, m. 171-3.5.degree.. I (0.01 mole) gave in the same fashion with the (-)-isomer of XVII 1.4 g. (-)-isomer (XIX) of XVIII, m. 107-9.degree., [.alpha.]D 52.2 .+-. 0.8.degree. (c 5, abs. EtOH). XIX (1.2 g.) stirred 2 weeks at room temp. with 5.5 g. (CO₂H)₂ and 40 cc. H₂O, the mixt. evapd., and the residue chromatographed on Al₂O₃ gave an inactive ketone fraction. I (3.4 g.) in 50 cc. dry C₆H₆ refluxed 5 min. with 2.1 g. (+)-5-(.alpha.-phenylethyl)semioxamazide and a crystal of iodine, the soln. concd. and cooled, and the product recrystd. from hexane-C₆H₆ gave
(+)-5-(.alpha.-phenylethyl)semioxamazone (XX) of I, soft needles, m. 108-9.degree., [.alpha.]D 107.2 .+-. 1.degree. (c 2); after 2.2 g. XX had been collected, the mother liquor evapd. to dryness, and the residue chromatographed on Al₂O₃ gave inactive I. XX gave also optically inactive I. I (9 g.) in 10 cc. Et₂O reduced in the usual manner with 2 g. LiAlH₄ in 40 cc. Et₂O, the mixt. treated with about 10 cc. H₂O and worked up, the resulting crude II (10 g.) treated with 8.8 g. phthalic anhydride, the mixt. heated 12 hrs. in 20 cc. dry PhMe at 110.degree., and the crude product recrystd. gave 14 g. acid phthalate (XXI) of II, m. 111-12.degree.. XXI (18 g.) and 7.07 g. (+)-Me-PhCHNH₂ (XXII) in 65 cc. Me₂CO warmed gently to soln., the soln. kept at room temp., and the cryst. deposit (20 g.) fractionally crystd. from Me₂CO gave 5 g. (+)-XXI-(+)-XXII salt, fine needles, m. 126-9.5.degree., [.alpha.]D 8.0 .+-. 1.degree. (c 5), which dissolved in the min. amt. of warm EtOH, treated with a large excess 10% aq. HCl, and cooled gave 3.5 g. (+)-XXI, m. 120-1.5.degree., [.alpha.]D 8-9.degree. .+-. 0.8 (c 6); the combined Me₂CO mother liquors acidified gave 13.7 g. XXI enriched in the (-)-isomer; it gave treated with 5.4 g. (-)-isomer (XXIII) of XXII 6.9 g. (-)-XXI-(-)-XXII salt, m. 127-9.degree., [.alpha.]D -9.4 .+-. 0.9.degree. (c 5) (fractionally crystd. from Me₂CO); the active salt treated with dil. HCl gave 4.3 g. (-)-XXI, colorless prisms, m. 120.5-1.5.degree., [.alpha.]D -10.0 .+-. 1.degree. (c 6); the mother liquors treated with dil. HCl gave 8.5 g. XXI enriched in the (+)-isomer and the (+)-enriched XXI (8.5 g.) resolved again in the same manner gave an addnl. 1.5 g. (+)-XXI and 1.9 g. (-)-XXI. (+)-XXI (4.6 g.) refluxed 2 hrs. with 40 cc. 25% aq. NaOH, the mixt. extd. with pentane, the ext evapd., and the residual crude product (2.35 g.) distd. gave (+)-II, b₂ 76-7.degree., m. 15-17.degree., n_D25 1.4805, [.alpha.]D 29.2 .+-. 0.4.degree. (c 11). (-)-XXI (6.1

g.) hydrolyzed in the same manner gave 3.02 g. (-)-II, b2 75.degree., m. 16-17.degree., nD25 1.4805, [.alpha.]D -30.4 .+- . 0.4.degree. (c 11). (+)-II (1 g.) treated in the usual manner with phthalic anhydride yielded 1.8 g. (+)-XXI, m. 120-1.degree., [.alpha.]D 8.7 .+- . 0.8.degree. (c 6). (-)-II (2 g.) in 15 cc. Me2CO treated dropwise with swirling with the calcd. amt. CrO3 soln. (1 drop excesss), the mixt. kept 10 min. at room temp., dild. with 20 cc. H2O, and extd. quickly with pentane gave 2 g. I, [.alpha.]D 0.degree., nD25 1.4696, which treated with XVII gave XVIII, m. 107-9.degree., [.alpha.]D -52.5 .+- . 0.8.degree. (c 5, abs. EtOH). (+)-II (1 g.) gave 0.9 g. inactive I.

IT 61265-62-1, Cyclononanone, 5,5-dimethyl-
(prepn. of)

RN 61265-62-1 HCAPLUS

CN Cyclononanone, 5,5-dimethyl- (9CI) (CA INDEX NAME)



IT 61265-62-1, Cyclononanone, 5,5-dimethyl-
(prepn. of)

L28 ANSWER 13 OF 15 HCAPLUS COPYRIGHT 2003 ACS on STN

1956:44331 Document No. 50:44331 Original Reference No.

50:8484h-i,8485a-d Many-membered carbon rings. XI. Civetone homologs. Blomquist, A. T.; Wolinsky, Joseph (Cornell Univ., Ithaca, NY). Journal of the American Chemical Society, 77, 5423-4 (Unavailable) 1955. CODEN: JACSAT. ISSN: 0002-7863.

AB cf. C.A. 50, 2454a. LiAlH4 (0.19 g.) in 50 cc. dry Et2O added to 0.5 g. 1,9-cyclohexadecanedione (I) in Et2O, the mixt. treated after 5 min. with 25 cc. H2O, the Et2O layer evapd., and the residue sublimed gave 0.47 g. 1,9-cyclohexadecanediol (II), white crystals, m. 104.5-106.degree.. 9-Hydroxycyclohexadecanone (III) (4.83 g.) gave similarly 4.58 g. 1,10-cyclooctadecanediol, white crystals, m. 130-1.5.degree. (from CHCl3-pentane). I (0.503 g.) in AcOH hydrogenated over 70 mg. prereduced Adams catalyst, the catalyst and the AcOH removed in vacuo, and the solid residue treated with about 60 cc. hexane at room temp. gave 0.07 g. crude II, m. 102-6.degree.; the mother liquor cooled to 0-5.degree. gave 0.22 g. III, m. 75-7.degree.; the remaining hexane soln. chromatographed on Magnesol-celite, and the column eluted with pentane-C6H6 gave 0.09 g. I, m. 75-80.degree.; further elution with CHCl3-C6H6 gave 0.09 g. III, m. 68-74.degree., fine fluffy needles. 1,10-Cyclooctadecanedione (IV) (0.81 g.) in AcOH hydrogenated partially, the catalyst and AcOH removed, the residue dissolved in hexane, the soln. chromatographed on Al2O3, and the column eluted with hexane-C6H6 gave 0.23 g. unchanged IV; further elution with

hexane-C₆H₆ gave 0.23 g. 10-hydroxycyclooctadecanone (V), m. 54-5.degree.; final elution with CHCl₃ gave 0.16 g. solid, m. 128-30.degree.. V, m. 54-5.degree., resolidified and remelted at 80-1.degree.; another sample of V recrystd. from pentane showed only m.p. 80-1.degree.. V gave a semicarbazone, m. 157.5-59.degree. (from MeOH). III (170 mg.) and 1.5 g. KHSO₄ heated 5 min. at about 250.degree., the cooled mixt. extd. with pentane, the ext. evapd., the residual oil dissolved in MeOH, and the soln. treated with H₂NCONHNH₂.HCl and NaOAc gave 145 mg. semicarbazone (VI) of 8-cyclohexadecen-1-one (VII), m. 168-70.degree. (from MeOH). VI (90 mg.) treated with aq. (CO₂H)₂ in the usual manner gave 60 mg. VII, colorless liquid, m. 17-22.degree.. V (155 mg.) fused with 2 g. KHSO₄ gave by direct sublimation crude 9-cyclooctadecen-1-one, which resublimed yielded 95 mg. pure material, waxy solid, m. 40-1.degree.; semicarbazone, m. 174-5.degree. (from MeOH).

IT 61265-62-1, Cyclononanone, 5,5-dimethyl-
(prepn. of)
RN 61265-62-1 HCAPLUS
CN Cyclononanone, 5,5-dimethyl- (9CI) (CA INDEX NAME)



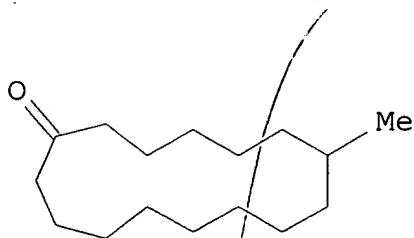
IT 61265-62-1, Cyclononanone, 5,5-dimethyl-
(prepn. of)

L28 ANSWER 14 OF 15 HCAPLUS COPYRIGHT 2003 ACS on STN
1935:8417 Document No. 29:8417 Original Reference No.
29:1071h-i,1072a-e Carbon rings. XVIII. The preparation of 2-methyl-, 3-methyl- and 7-methyl-1-cyclopentadecanone. Supplement to the synthesis of dl-muscone. Ruzicka, L.; Stoll, M. Helvetica Chimica Acta, 17, 1308-18 (Unavailable) 1934. CODEN: HCACAV. ISSN: 0018-019X.

AB cf. C. A. 28, 4708.9. The prepn. of .alpha.-, or .beta.-methyl-1-cyclopentadecanone (muscone) could not be carried out by the usual methods of heating rare earth salts of the suitable Me tetradecanecarboxylic acids. Other methods were attempted. The oxidation of cyclopentadecene with CrO₃ in AcOH gave a small amt. of 2-cyclopentadecen-1-one (I) (semicarbazone, m. 210-20.degree.). CrO₃, in Ac₂O-AcOH and 1-methyl-1-cyclopentadecene (II) produced 2-, or 3-methyl-2-cyclopentadecen-1-ol (III), b₁ 150-1.degree., which was purified through the phthalate. When II was oxidized with SeO₂ in boiling MeOH, 2-methyl-2-cyclopentadecen-1-one (IV), b_{0.2} 119-29.degree., was obtained and reduced to 2-methylcyclopentadecanone (V) (semicarbazone, m. 148.5-9.5.degree.) with Ni and H₂. Exaltone and Br₂ formed 1-bromocyclopentadecanone (VI), b_{0.00} 126-34.degree.. The removal of HBr from VI gave I,

b0.04 113-18.degree., d422 0.9320, nD22 1.4902. VI was treated with sodiomalonic ester to form di-Et 1-(3-ketocyclopentadecyl)malonate (VII), b0.11 190-200.degree., d420 1.020, nD20 1.4787. VII was converted to the malonic acid, m. 140-1.degree., which at 180.degree. lost CO₂, forming 1-(3-ketocyclopentadecyl) acetic acid (VIII), m. 89-90.degree.. The electrolysis of the Na salt of VIII in MeOH gave .alpha.,.beta.-bis [1-(3-ketocyclopentadecyl)] ethane, m. 104.degree., and muscenone which was reduced with Ni and H₂ to dl-muscone (IX). The alc. reduction mixt. gave a semicarbazone, m. 170-1.degree., and the semicarbazone of IX, m. 143.4.degree.. Finally IX was prepd. by Ziegler's method from 2-methyl-1,14-dicyanotetradecane, b2 248-9.degree.. IX from this prepn. gave a semicarbazone, m. 136-7.degree., which with PhNH₂ formed a phenylsemicarbazone, m. 170-1.degree.. The semicarbazone of natural muscone m. 141-3.degree., and the phenylsemicarbazone m. 158-60.degree.. Further evidence was presented to show that mixed m. ps. could not be relied upon with semicarbazones of this series. The isomeric 7-methylcyclopentadecanone (X) was prepd. from di-Et 3-methylsuberate in the following steps; 4-methyl-1,8-octanediol, b2.6 128-33.degree. (Bouvealt reduction), 4-methyl-1,8-dibromooctane, b2 122-3.degree., di-Me 5-methyldecane-1,10-dicarboxylate (malonic ester, and esterification), b10 180-7.degree., 6-methyl-1,12-dodecanediol, b12 185-93.degree., 6-methyl-1,12-dibromododecane, b16 198-203.degree., di-Me 7-methyltetradecane-1,14-dicarboxylate, b1 187-93.degree., the corresponding acid, m. 77-8.degree., its Ce salt, X (by dry distn.), b20 182-3.degree. (semicarbazone, m. 181-2.degree.).

IT 127818-69-3, Cyclopentadecanone, 7-methyl-
(and derivs.)
RN 127818-69-3 HCAPLUS
CN Cyclopentadecanone, 7-methyl- (9CI) (CA INDEX NAME)



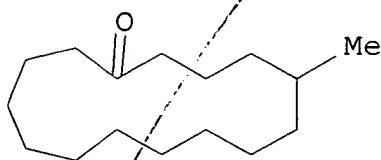
IT 127818-69-3, Cyclopentadecanone, 7-methyl-
(and derivs.)

L28 ANSWER 15 OF 15 HCAPLUS COPYRIGHT 2003 ACS on STN
1928:37634 Document No. 22:37634 Original Reference No.
22:4483g-i,4484a-g Carbon rings. XII. The preparation of methylated 14-, 15- and 17-membered cyclic ketones. Ruzicka, L.; Schinz, H.; Pfeiffer, M. (Utrecht Univ.). Helvetica Chimica Acta, 11, 686-700 (Unavailable) 1928. CODEN: HCACAV. ISSN: 0018-019X.
AB Since muscone is a 1-methylcyclopentadecan-3-one, attempts were made to prep. similar cyclic ketones with the Me group in a position 1, 2, 3 and 4 to the CO group and to compare the musk odors of such

comps. The method of prepn. consisted in heating the Th or Y salts of polymethylenedicarboxylic acids and it was found that only those comps. with the Me group in position 3 or 4 yielded cyclic ketones. 1,3-Dimethylcyclotridecan-2-one (5.4 g.) does not have a musk odor and was prepd. by destructive distn. of 173 g. of the Th salt of tetradecane-2,13-dicarboxylic acid (from the Na salt in H₂O and Th(NO₃)₄); the distillate was then redistd. at 12 mm., converted to semicarbazone in MeOH, which was sepd. and hydrolyzed to the ketone with concd. H₂C₂O₄; it b₁₂ 130.degree.-b₁ 170.degree.. An attempt to prep. 1-methylcyclotridecan-3-one from the Th salt of 2-methyldodecane-1,12-dicarboxylic acid was not successful, yielding a mixt. of products which were not completely sepd. and did not have a musk odor; 1-methylcyclotetradecan-2-one could not be prepd. from the Y salt of tetradecane-1,13-dicarboxylic acid and the product of distn. did not have a musk odor. 1-Methylcyclotetradecan-4-one, m. 28-9.degree., which has a musk odor was prepd. by heating to 170-80.degree. the Y salt of 3-methyltridecane-1,13-dicarboxylic acid (133 g.); the 59 g. of product thus obtained was fractionated as follows: (a) 10 g., b₁₂ 65-130.degree.; (b) 4 g., b₁₂ 130-50.degree.; (c) 2.2 g., b₁ 120-40.degree. (d) 5.5 g., b₁ 140-60.degree.; (e) 2.8 g., b₁ 160-80.degree.; all of these fractions were converted to the semicarbazone (d yielding the most), m. 182-3.degree.; from the mother liquors the semicarbazone of Me .omega.-methyltridecyl ketone was obtained, m. 118-9.degree.. An attempt to prep. 1-methylcyclopentadecan-2-one from the Th salt of pentadecane-1,14-dicarboxylic acid was not successful and did not give products with a musk odor. 1-Methylcyclopentadecan-2-one was prepd. by adding 4 g. cyclopentadecanone in 100 cc. abs. Et₂O to 4 g. finely divided NaNH₂ under PhH and cooled with ice, allowed to stand several hrs., then shaken 2 days at room temp. The flocculent Na deriv. of the ketone was decanted with the liquid from the solid residue of NaNH₂, which was washed with abs. Et₂O, the Et₂O suspension boiled 2 days with excess MeI, treated with H₂O and distd., b₁₂ 171-3.degree., converted to semicarbazone (m. 149-50.degree.) and then the ketone was regenerated from the latter with H₂C₂O₄; the odor is similar but slightly less than the unmethylated ketone, d₄₁₆ 0.9213, n_{D16} 1.4812, MD 73.60. 1,3-Dimethylcyclopentadecan-2-one could not be prepd. by distn. of the Y salt of hexadecane-2,15-dicarboxylic acid and the product of distn. did not have a musk odor. Attempts to prep. 1-methylcyclopentadecan-3-one (dl-muscone) from the Th salt of 2-methyltetradecane-1,14-dicarboxylic acid were not successful but gave a product which is probably Me .omega.-methyltetradecyl ketone, forming a semicarbazone, m. 122.degree.; similarly the Y salt yielded the same semicarbazone (m. 122.degree.) and another semicarbazone which is probably the isomer, m. 83.degree.; regeneration of the ketones from the mother liquors gave an oil with a strong musk odor indicating the presence of traces of dl-muscone. Distn. of the Y salt of 2,13-dimethyltetradecane-1,14-dicarboxylic acid did not yield 1,5-dimethylcyclopentadecan-3-one but gave a very small amt. of Me 2,3-dimethyltetradecyl ketone which was isolated as the semicarbazone, m. 78-9.degree.; the distillate had a very slight

musk odor. 1-Methylcyclopentadecan-4-one was prepd. by heating the Th salt of 3-methyltetradecane-1,14-dicarboxylic acid (from 81 g. acid) which yielded 50 g. of distillate and when fractionated gave: (a) 4 g., b12 45-90.degree.; (b) 7.2 g., b12 90-150.degree.; (c) 10.7 g., b0.5 120-60.degree.; (d) 3 g., b0.5 160-80.degree.; (e) 4.2 g., b0.5 180-205.degree.; (f) 8 g., b0.5 205-50.degree.. Fraction c has a decided musk odor and yields the greatest quantity of semicarbazone, m. 161-2.degree., although the latter could be obtained from all fractions; the ketone regenerated from the semicarbazone, b0.5 125.degree. and has an odor which cannot be distinguished from muscone. Distn. of the Th salt of 4-methyltetradecane-1,14-dicarboxylic acid gave 1-methylcyclopentadecan-5-one, which was isolated as the semicarbazone, m. 164.degree.. Methylation of dihydrocibetone gave 1-methylcycloheptadecan-2-one, which b0.5 150.degree. and has an odor that can hardly be distinguished from the unmethylated ketone; the semicarbazone, m. 142-3.degree.. 1-Methyl-cyclopentadecan-1-ol, m. 85-6.degree., was prepd. by the Grignard reaction from cyclopentadecanone (10 g.) and MeI (5 g.); at the same time a small amt. of compd., m. 162.degree., was obtained and this is probably a dimol. cyclopentadecanone (C₃₀H₅₆O₂) or a pinacone (C₃₀H₅₈O₂); when the methylcyclopentadecanol was dehydrated by heating several hrs. with 90% HCO₂H it gave almost quant. 1-methylcyclo-1-pentadecane, b12 152-3.degree., d₄₂₂ 0.8697, n_{D22} 1.4853, MD 73.26; reduction with H and Pt black in EtOAc gave methylcyclopentadecane, b12 147-8.degree., d₄₂₁ 0.8576, n_{D21} 1.4735, MD 73.34.

IT 135522-51-9, Cyclopentadecanone, 5-methyl-
(prepn. of)
RN 135522-51-9 HCAPLUS
CN Cyclopentadecanone, 5-methyl- (9CI) (CA INDEX NAME)



IT 135522-51-9, Cyclopentadecanone, 5-methyl-
(prepn. of)